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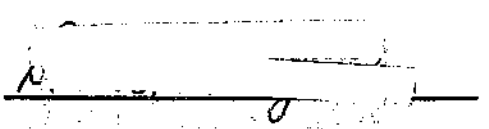

MEASUREMENT OF WATER VAPOR CONTENT OF AIR-WATER VAPOR MIXTURES AT LOW VACUUM PRESSURES

A THESIS

Presented to

The Faculty of the Graduate Division

by

David Fairfield Dyer

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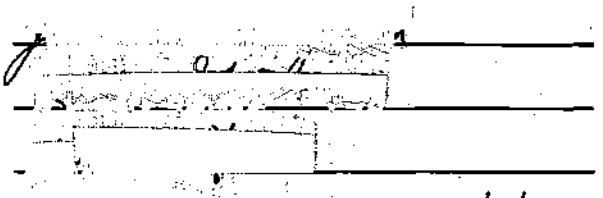
Approved:



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SUMMARY

A standard was developed such that moisture content of air-water vapor mixture could be determined at low vacuum pressures. The operation of the standard involved measuring the pressure and temperature of an air-water vapor mixture; then freezing the water vapor from the mixture and again measuring the pressure and temperature. The specific humidity, relative humidity, and partial density were calculated from their defining equations. The equations were reduced by application of the ideal gas law to a form involving only the quantities measured with the standard. Thus, a direct substitution of the measured values from the standard into the reduced equations yielded the values of the desired terms.

Three types of hygrometric devices were experimentally checked with the standard as a possible means of determining water vapor content under low vacuum conditions. These devices were: temperature of ice in quasi-static equilibrium with an air water vapor mixture, pressure of air-water vapor mixture read through a liquid nitrogen cold trap, and an electrolytic humidity transducer.

The ice temperature showed a sensitivity to the surrounding moisture content of the air-water vapor mixture, but the equipment used did not control all of the factors governing the ice temperature closely enough to obtain repeatable calibrations.

It was determined that the pressure of an air-water vapor mixture read through a liquid nitrogen cold trap was greater than the dry air

partial pressure but less than the total pressure of the mixture in the millimeter of mercury pressure range.

A successful calibration of a Phys-Chemical Research Corporation model number 11 humidity transducer was made. The calibrations were done for a total pressure range of 2 to 5.47 millimeters of mercury and a specific humidity range of approximately 0 to 1.0. The transducer was found to be temperature sensitive and the temperature coefficient of the transducer was determined to be essentially independent of pressure and approximately equal to 0.2 per cent relative humidity per ^{o}F for a temperature range of 63 to 93^{o} F. The gage was also sensitive to total pressure. Calibrations were made at 2.0, 3.5, and 5.47 millimeters of mercury, and an equation was developed such that for any pressure in this range the specific humidity could be determined from knowledge of the total pressure and humidity transducer resistance. The maximum probable error in the calibration curves for the transducer was found to be 5 per cent.

NOMENCLATURE

Symbol		Units
A(p)	pressure coefficient	dimensionless
B(p)	pressure coefficient	dimensionless
C	capacitive impedance	meg ohms
E	electrical voltage	volts
I	electrical current	amps
L	partial density	lbm/ft^3
m	mass	lbm
M	molecular weight	lbm-mole
$\bar{P}$	partial pressure	lb/ft^2
P	total static pressure	lb/ft^2
R	gas constant	ft-lbf/lbm R
R	electrical resistance	meg ohms
T	temperature	^oF
v	specific volume	ft^3/lbm
V	volume	ft^3
w	specific humidity	lbm air
Z_{equi}	equivalent impedance	meg ohms
Greek Letters		
δ	differential	
Φ	relative humidity	lbm water
Subscripts		
1	before freezing out water vapor	

2	after freezing out water vapor
a	air
f	final
i	initial
in	input
s	saturation
sh	shunt
w	water
x	property valve measured across transducer

CHAPTER I

INTRODUCTION AND HISTORICAL BACKGROUND

Statement of Intent

The intent of this study is to develop a means of experimentally determining water vapor content of an air-water vapor mixture under low vacuum conditions. A standard for calibrating hygrometric devices is described and used to calibrate convenient instrumentation for making the desired measurement.

Psychrometric Measurements

Two important terms which arise in describing the quantity of water in a given amount of air are the relative humidity and the specific humidity. Although these terms are used quite commonly, they have been widely misinterpreted; and it is felt that a brief explanation of these terms would be valuable in interpreting the results of this work.

Consider two closed volumes shown in Figure 1. Volume A contains a quantity of water in excess of the amount required to saturate it at the existing temperature "T," and volume B contains water in the unsaturated state also at the temperature "T." Both volumes contain no other permanent gas. A natural definition of relative humidity follows these considerations. If the volumes of the saturated and unsaturated vapor are assumed equal, then the percentage ratio

$$\frac{m}{m_s} 100 \equiv \Phi \qquad (1.1)$$

is defined as the relative humidity where "m" and "m_s" denote the mass of vapor in volume B and A respectively.

From application of the law of perfect gases, the following relations can be written

$$P \cdot V = m R T \qquad (1.2a)$$

$$P_s \cdot V = m_s R T \qquad (1.2b)$$

On substitution of equations 1.2a and 1.2b into equation 1.1 and simplifying, an alternate form of the definition of relative humidity for gases obeying the ideal gas law can be deduced

$$\Phi = \frac{P}{P_s} 100 \qquad (1.3)$$

Volume A Volume B

Figure 1. Definition of Relative Humidity

This is the commonly used form of the definition. If a permanent gas is introduced into the volume, P in the equation is taken as the partial pressure of the water vapor ($\bar{P}w$). It should be carefully noted that the introduction of a permanent gas could make equation 1.3 invalid. This occurs because the second gas begins to affect the water vapor pressure with an increasing effect with increased pressure due to deviation from the ideal gas laws at high pressures. Since secondary gases at low pressures are the concern of this work, equation 1.3 can be taken as valid within the limits of the experimental accuracy for this work.

The term specific humidity merely denotes the ratio of the mass of water to the mass of air in a given volume. Notice that this term is not the same as the mass fraction of vapor (mass of vapor divided by the total mass of the mixture).

Historical Background (1)

Psychrometric measurement has become a subject of significance only in this century. Earlier the chief interest lay in meteorological practice, in which the hair and dew point hygrometers were used. Since that time many different needs for humidity measuring devices under extreme conditions have arisen. In fact, the impetus behind this work is the desire to measure concentration gradients between meat and its environment under freeze drying conditions.

The first hygrometer was invented by Leonardo da Vinci around the year 1500. Using the principle that wool absorbs water, Leonardo proposed letting the wool form one arm of an elementary mass balance

apparatus. As the moisture content of the air increased, the wool weight would increase due to absorption of water. This change was recorded by movement of a pointer over a graduated scale. Nothing of note is recorded concerning hygrometry in the subsequent 150 years. In the succeeding years two new hygrometric devices were suggested: a dew point hygrometer and a timber hygrometer based on the fact that wood expands on absorbing moisture.

In 1750 Richman observed that a thermometer whose bulb was wetted indicated a lower temperature than the temperature of the surroundings recorded with a dry bulb thermometer. Cullen in 1755 explained this fact as the effect of evaporation of water and, thus, initiated the wet and dry bulb psychrometer.

In 1773 De Luc produced a hygrometer which consisted of a strip of whale bone which by its changes in length with humidity indicated humidity by movement of a pointer over an index. About this same time De Saussure invented his famous hair hygrometer which is still quite useful today. A disagreement arose between De Saussure and De Luc over the proper calibration point for the extreme wet condition. De Luc proposed that immersion of the strip of whale bone into water would be the proper procedure for calibration, but De Saussure maintained that the hygrometer should be calibrated for the extreme wet condition in a jar inverted over water with the walls of the jar wetted frequently. De Saussure substantiated his statement by showing that the hair was a few per cent shorter immersed in water than in the jar described above. That the idea of "relative humidity" was beginning to form at this time is shown by this statement by Von Arnim given in

reference (2): "When we remark on the dryness of air we can not define such a condition as the absolute moisture content, but only of the relative amount or degree of saturation." Also around the year 1800 Leslie worked on a basis for psychrometry, and Dalton determined the relationship between water vapor and dry air pressure with his law of partial pressures. Thus, a new era of hygrometry was initiated.

Many improvements of the earlier crude instruments were made in the nineteenth century with considerable effort expended at analytically predicting humidity from Du Saussure's hair hygrometer, the wet bulb measurement, and the dew point apparatus.

No practical new methods for hygrometric measurements were proposed until the 1930's when Dunsmore in the United States and Gregory in England started working on an electrolytic hygrometer. In the last twenty years two useful types of hygrometers have been proposed: Jason's capacitance hygrometer and Wylie's hygrometer, a special type of electrolytic hygrometers. The principle of operation of these devices will be discussed in the next section.

In summary, although many types of hygrometeric devices have been proposed, the ideal hygrometer has not yet been found. This is substantiated by Gregory and Rourke (2): "The ideal hygrometer has not yet been evolved and its evolution would seem to depend upon the discovery of a physical phenomena dependent solely on humidity and with equal sensitivity at dryness or saturation."

Hygrometric Instruments

Although an understanding of the various types of hygrometric devices is not essential for following this work, it is felt that a

basic knowledge of their mode of operation will furnish the reader with a better appreciation of the difficulty of making the desired measurements. Therefore, the principle of operation for five important types of hygrometric devices will be considered.

Wet and Dry Bulb Hygrometer

Basically the instrumentation of this device consists of two mercury in glass thermometers. One of these thermometers has a wetted fabric placed over the bulb, and the air sample under consideration is blown over this bulb. It is found that the equilibrium temperature for this bulb is a function of the moisture content of the air (i.e. water concentration gradient), pressure of the sample, and the temperature of the sample taken with the dry bulb thermometer. Although the instrument has been popular for many years, the theoretical background in regard to the relation of the vapor pressure of the water in a moist atmosphere to the wet bulb depression is unsatisfactory. Consequently, charts obtained from experiments are plotted for the wet bulb depression versus the relative humidity of the atmosphere, and these charts are used to determine the relative humidity from the reading of the wet and dry bulb hygrometer. For the pressures of concern in this work, it is found that the wetted bulb freezes and no successful experimental work has been done in this area (see Chapter IV).

Electrolytic Hygrometers

The basic hardware of this type of instrument consists of some material whose surface is impregnated with a hygroscopic salt. The electrical resistance of the salt changes with change in moisture content and a calibration can be determined between temperature, pressure,

moisture content, and electrical resistance. This is the type of transducer used for this work. (See Chapter III for further discussion of this type hygrometer).

Diffusion Hygrometer

For ease of explanation the basic construction of this instrument is shown in Figure 2. It consists essentially of a closed container fitted with a manometer, and a fine grained porous clay plate. The inside of the container is kept dry with an efficient drying agent. Using Knudsen's law of molecular streaming it can be shown theoretically that the water vapor and air diffuse at different rates through the clay plate which results in a pressure difference between the inside and outside of the container. This pressure difference can be related to the external moisture content, and, thus, with this relationship and the pressure difference indicated by the manometer on the diffusion hygrometer, the external water vapor content can be calculated. The

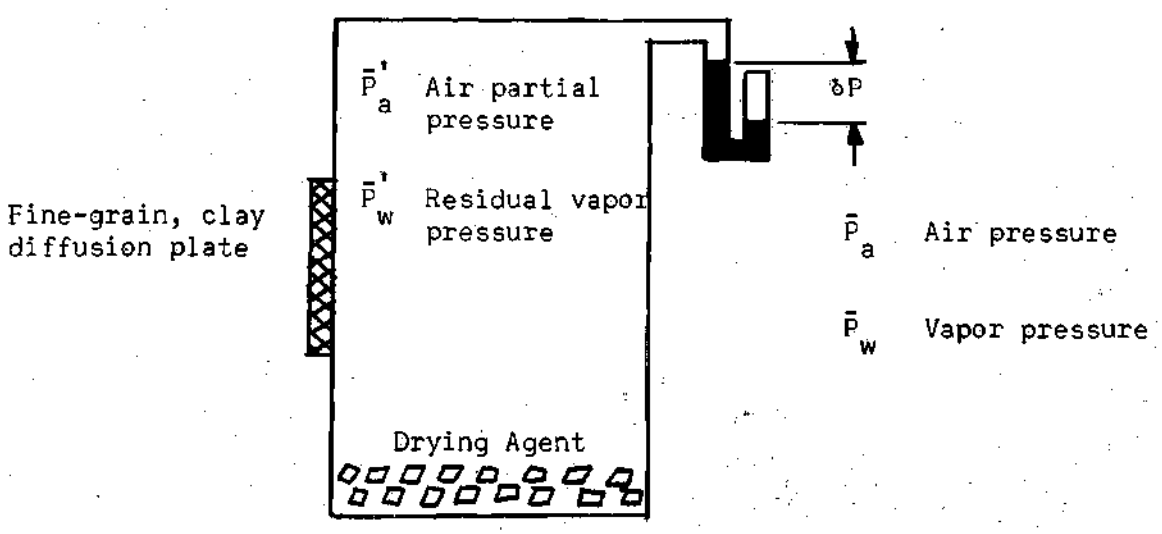

Figure 2. Diffusion Hygrometer

theoretical work for the instrument checks closely with experiment at one atmosphere pressure but the sensitivity of this instrument for small mass concentrations differences such as are found in this work would not be sufficient.

Dew Point Hygrometer

When moist air is cooled down at a constant pressure, the water in the air will tend to condense when the temperature reaches the saturation temperature of the water vapor. But since the air-water vapor mixture was cooled at a constant pressure, the partial pressure of the water vapor remains constant, and, therefore, the original partial pressure of the water is equal to the saturation pressure at the temperature at which condensation began. With this information and the original temperature of the air-water vapor mixture, the relative humidity can be calculated from equation 1.3. This is the basis of the dew point hygrometer although many different types of instruments are used to produce the constant pressure cooling and to detect the temperature of condensation.

Capacitance Hygrometer

It is a well known physical fact that the permittivity of a material is a function of the water content of the material. The operation of the capacitive hygrometer is based on this fact. The instrument consists essentially of parallel plates separated by a hygroscopic material. As the material absorbs water it changes the permittivity and thus the capacitance between the two plates. A calibration curve of capacitance versus moisture content of the hygroscopic material can be obtained. This instrument has a serious drift problem associated

with it which at the present time is not fully understood; and, therefore, it would not be practical at low humidities (reference 10).

Purpose and Scope

The purpose of this experimental work is to find some convenient type of instrumentation for measurement of moisture content under low vacuum conditions. Once this instrument is found it will be used in conjunction with a standard to generate a calibration curve of moisture content versus instrument read-out for the desired conditions of pressure, temperature, and per cent water.

CHAPTER II

ANALYTICAL INVESTIGATIONS

Mathematical Statement of Problem

Figure 3 depicts a standard for determination of water vapor content. The process consists of isolating a volume "V" of an air-water vapor mixture at a measured pressure and temperature. The container used to isolate the volume under consideration is then immersed in a liquid nitrogen bath which causes the water vapor to freeze out on the inside surface of the container. It is assumed that the frozen water has a negligible volume. The pressure and temperature inside the tank after immersion of the container in liquid nitrogen are again measured.

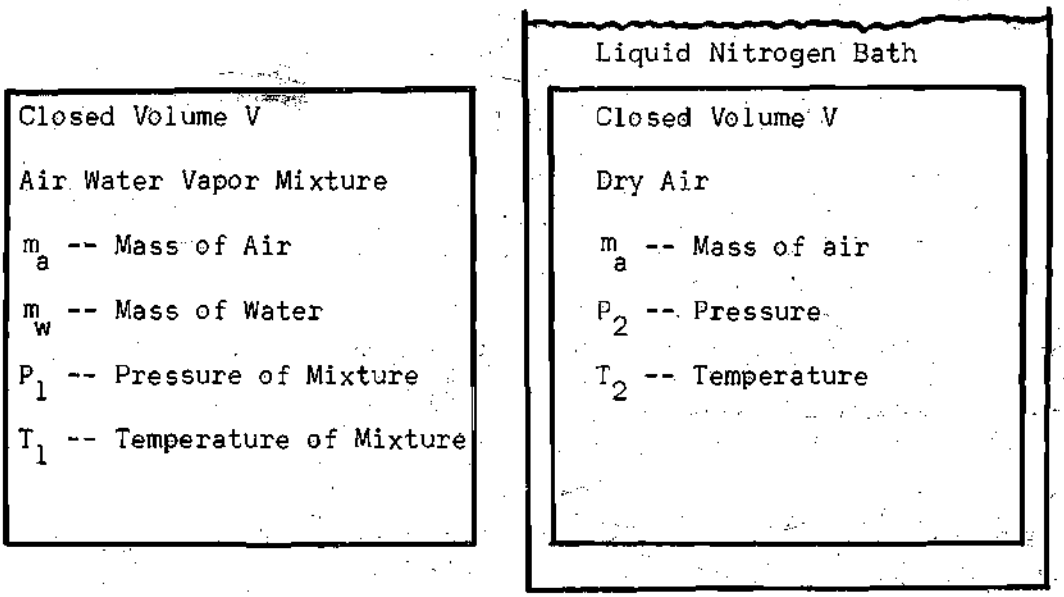

Figure 3. Humidity Standard

It is desired to calculate the specific humidity, relative humidity, and partial density of the air-water vapor mixture from the measurements made with the aid of the standard. These measurements were: 1. The temperature and pressure of an air-water vapor mixture contained in a fixed volume "V," and 2. The temperature and pressure of the air originally contained in the mixture after the water vapor has been frozen out by immersion of the container in liquid nitrogen.

The governing equations for this problem are the ideal gas law,

$$m = \frac{PV}{RT} \tag{2.1}$$

Dalton's law of partial pressures,

$$\bar{P}_a + \bar{P}_w = P \tag{2.2}$$

and the definitions of relative humidity, specific humidity and partial density:

$$\Phi = \bar{P}_w / P_s = 100 \tag{2.3a}$$

$$w = m_w / m_a \tag{2.3b}$$

$$L = m_w / V \tag{2.3c}$$

Reduction of Governing Equations

The mass of the air after the water vapor has been frozen from the mixture can be calculated from equation 2.1.

$$m_a = \frac{P_2 V}{R_a T_2} \tag{2.4}$$

The definition of the partial pressure as the pressure that a component of a mixture would exert if it existed alone at the volume and the temperature of the mixture is utilized with equation 2.1 to compute the partial pressure of the air in the original mixture as follows:

$$\bar{P}_a = \frac{m_a R_a T_1}{V} \tag{2.5}$$

Substituting equation 2.4 into equation 2.5 and simplifying the following is obtained:

$$P_A = P_2 T_1 / T_2 \tag{2.6}$$

From equation 2.2 the partial pressure of the water vapor can be obtained as follows:

$$\bar{P}_w = P_1 - \bar{P}_a \tag{2.7}$$

On substitution of equation 2.6 into equation 2.7 the equation for the partial pressure of the water vapor becomes

$$\bar{P}_w = P_1 - P_2 T_1/T_2 \tag{2.8}$$

A usable form of the definition of relative humidity can be obtained by substituting equation 2.8 into equation 2.3a.

$$\Phi = \frac{P_1 - P_2\left(\frac{T_1}{T_2}\right)}{P_s} \cdot 100 \tag{2.9}$$

Note that P_s is the saturation pressure of water at the temperature "T." Its value can be found in reference (3).

Again using the definition of partial pressure in conjunction with equation 2.1, the mass of water vapor in the volume "V" can be determined as:

$$m_w = \frac{\bar{P}_w V}{R_w T_1} \tag{2.10}$$

Substituting equation 2.8 into equation 2.10, the following simplified form is obtained:

$$m_w = \frac{V(P_1/T_1 - P_2/T_2)}{R_w} \tag{2.11}$$

Substituting equations 2.4 and 2.11 into equation 2.3b, the following expression for the specific humidity is obtained:

$$w = \frac{R_a}{R_w}\left(\frac{P_1}{P_2}\frac{T_2}{T_1} - 1\right) \tag{2.12}$$

Noting that $R_a/R_w = 0.622$, equation 2.12 reduces to

$$w = .622\left(\frac{P_1}{P_2}\frac{T_2}{T_1} - 1\right) \tag{2.13}$$

which is a usable form of the definition.

To obtain a convenient form for the partial density, equation 2.11 is substituted into equation 2.3c and simplified to:

$$L = \frac{1}{R_w}\left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) \tag{2.14}$$

Noting that $1/R_w = 0.01168$ lbm $^{\circ}$R/ft-lbf, equation 2.4 reduces to the final form for the partial density.

$$L = 0.01168\left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) \tag{2.15}$$

Thus, from the measurements taken with the aid of the standard, the relative humidity, specific humidity, and partial density can be calculated analytically from equations 2.9, 2.13, and 2.15 respectively.

CHAPTER III

EXPERIMENTAL INVESTIGATIONS

Instrumentation and Equipment

Geometry

In order to calibrate the various humidity instruments, a standard had to be developed such that the read-out of the humidity instrument could be compared to the actual humidity determined from the standard. The basis for the standard used is shown in Figure 3. The following method of calibration is used in conjunction with the standard:

1. An air-water vapor mixture is isolated in a tank of fixed volume with the humidity sensing device located inside the tank and exposed to the mixture. The pressure and temperature of this mixture are then taken.

2. The tank is then submerged in a liquid nitrogen bath which freezes the water vapor from the mixture. The pressure and temperature are again measured.

3. By use of the equations developed in Chapter II, the moisture content is calculated from the measurements taken from the standard and compared with the humidity instrumentation read-out.

The following necessary conditions were considered in determining the geometrical configuration for the standard:

1. For the test to be valid there must be pressure, temperature, and composition equilibrium between all parts of the vacuum sample.

2. The tank volume should be large compared to the pressure instrumentation internal volume and should be sufficient to house the necessary instrumentation.

3. The mass of the tank which is to be surrounded with liquid nitrogen should be as small as possible.

In looking at the requirement of condition 1, preliminary heat transfer calculations were made which showed that the tank in which the water vapor was frozen out would have to be completely immersed in liquid nitrogen in order to obtain a uniform temperature of the vacuum sample. If only one tank were used to meet this requirement, it would be difficult to provide feed-throughs for the thermocouple and test humidity instrumentation wires, because these connection points would introduce local hot spots. In order to satisfy this requirement and also for convenience in setting up and carrying out a test, it was decided to use two tanks connected by a valve. One tank has as a purpose the housing of the humidity instrumentation and is hereafter designated tank I, and the other tank, designated tank II, is designed for submersion in liquid nitrogen. Using two tanks does not completely eliminate the problem of hot spots since the vacuum valve in the line connecting the two tanks could not be placed directly against tank II. This location was not possible because the rubber seats in the valve will not withstand cryogenic temperatures. Some error must be accepted here, but the volume between the valve and tank II should be held to a minimum.

In order to provide pressure and composition equilibrium between the two tanks, the connecting line must be much larger in diameter than the mean free path of the molecules in the vacuum sample. This is not a

stringent requirement because the mean free path at the pressure level involved (approximately one millimeter of mercury) is extremely small compared to ordinary pipe sizes.

Conditions 2 and 3 were not difficult to provide with the use of the two tanks. There was no maximum size dictated for tank I except from a cost standpoint. Its volume was made greater than ten times the internal volume of the pressure gage used (NRC model number 520 alphatron). The volume of tank II was made smaller than that of tank I for two reasons: the internal volume of the pressure gage used (Kinney model "Measurvac" gage) was much smaller than the alphatron, and in order to conserve liquid nitrogen for cooling down the mass of the tank.

The overall geometrical configuration of the equipment used is indicated in Figure 4, which is a photograph of the experimental set up. A schematic showing the arrangement of the equipment is given in Figure 5.

Mechanical Equipment

With the exception of the vacuum pump, the detailed machine drawings for the mechanical equipment are shown in Figures 6 through 8. This equipment consists chiefly of two large vacuum tanks connected by a one inch diameter valved line. A liquid nitrogen jacket is provided for tank II. The vacuum pump used is a Kinney model number KD-30 reciprocating vacuum pump connected to tank I by a one inch diameter rubber hose. A vacuum valve is provided between the pump and tank I. The pump capacity is thirty cubic feet per minute with a blank-off pressure of ten microns.

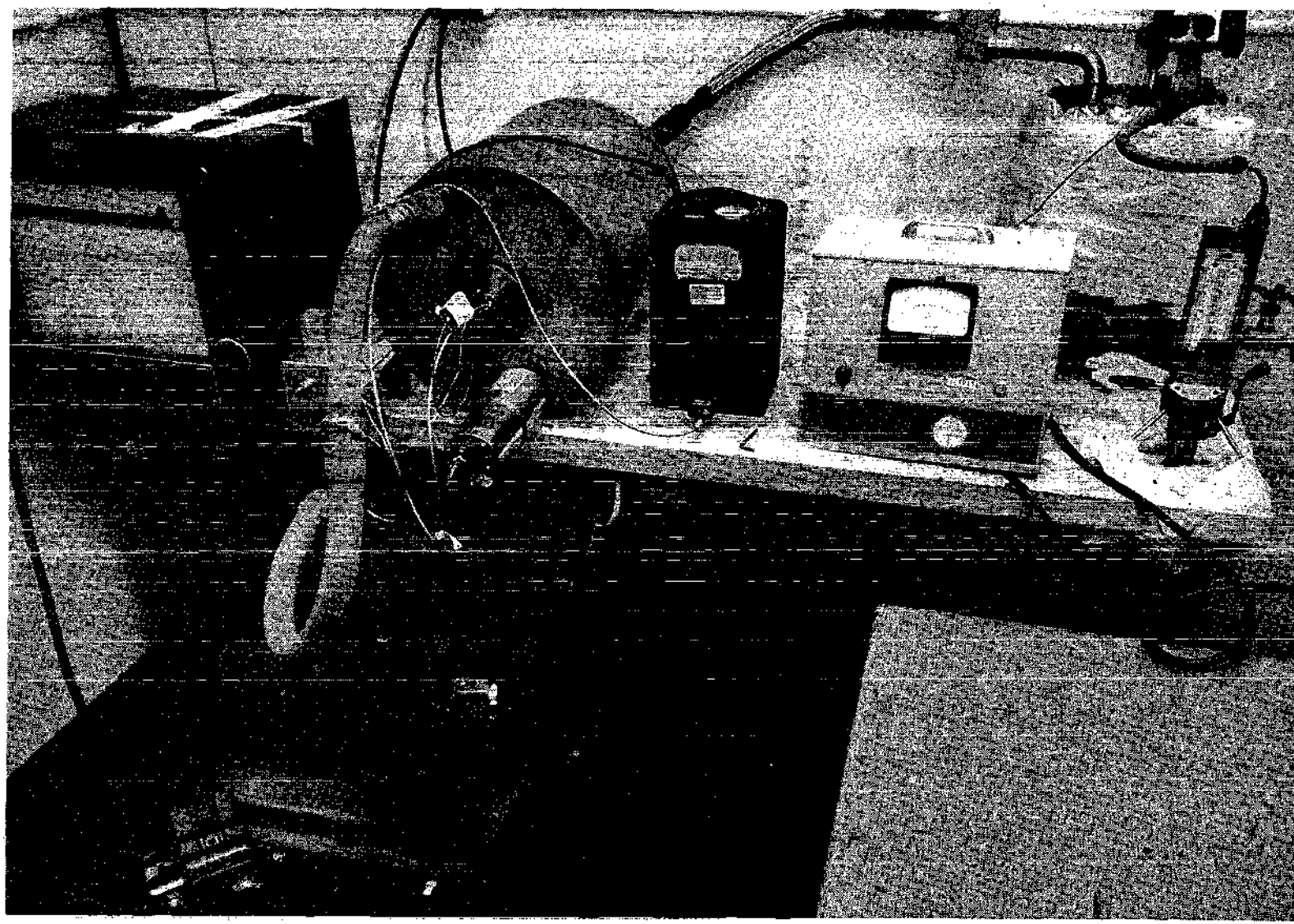

Figure 4. Experimental Apparatus

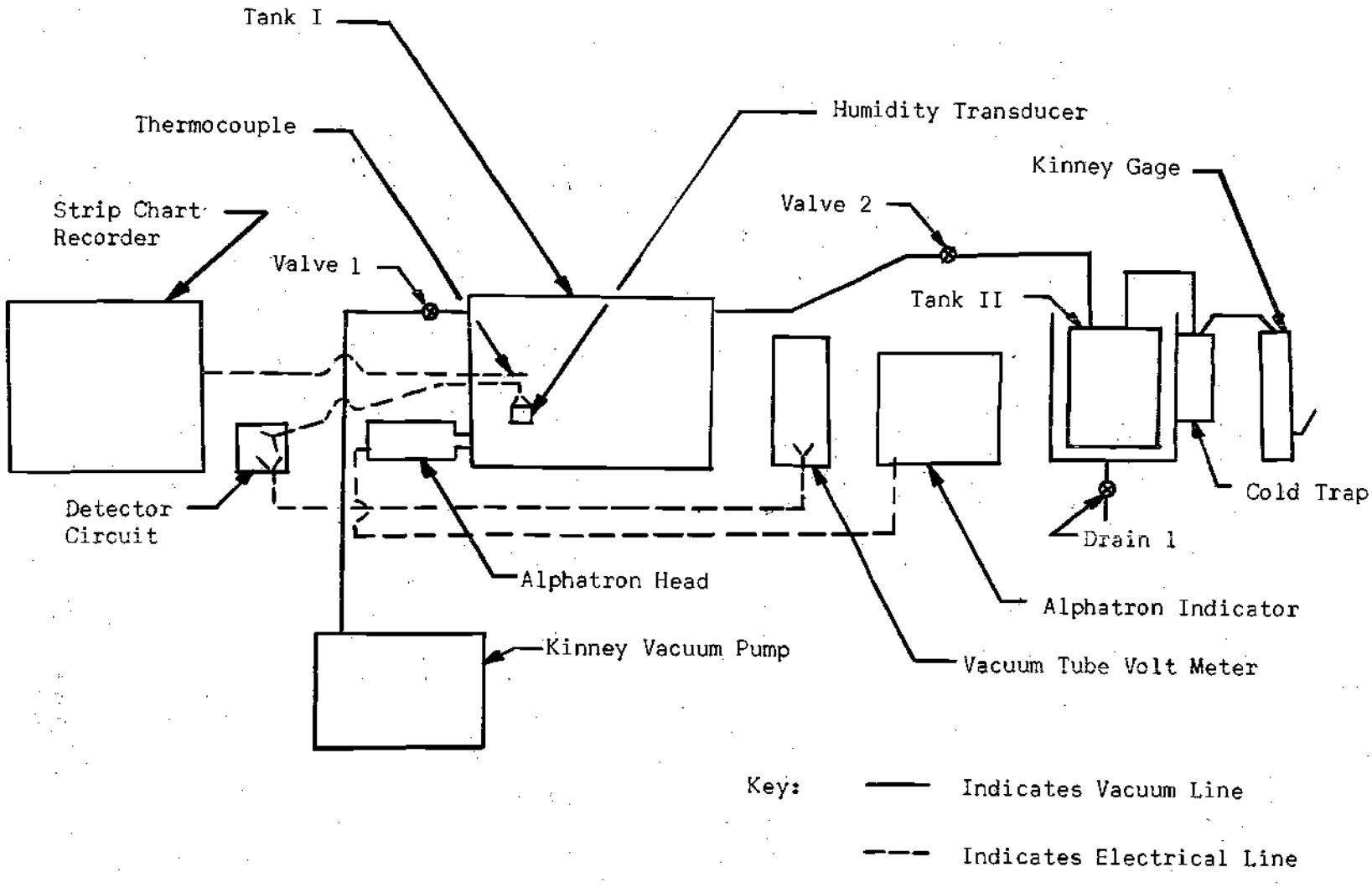

Figure 5. Schematic of Experimental Apparatus

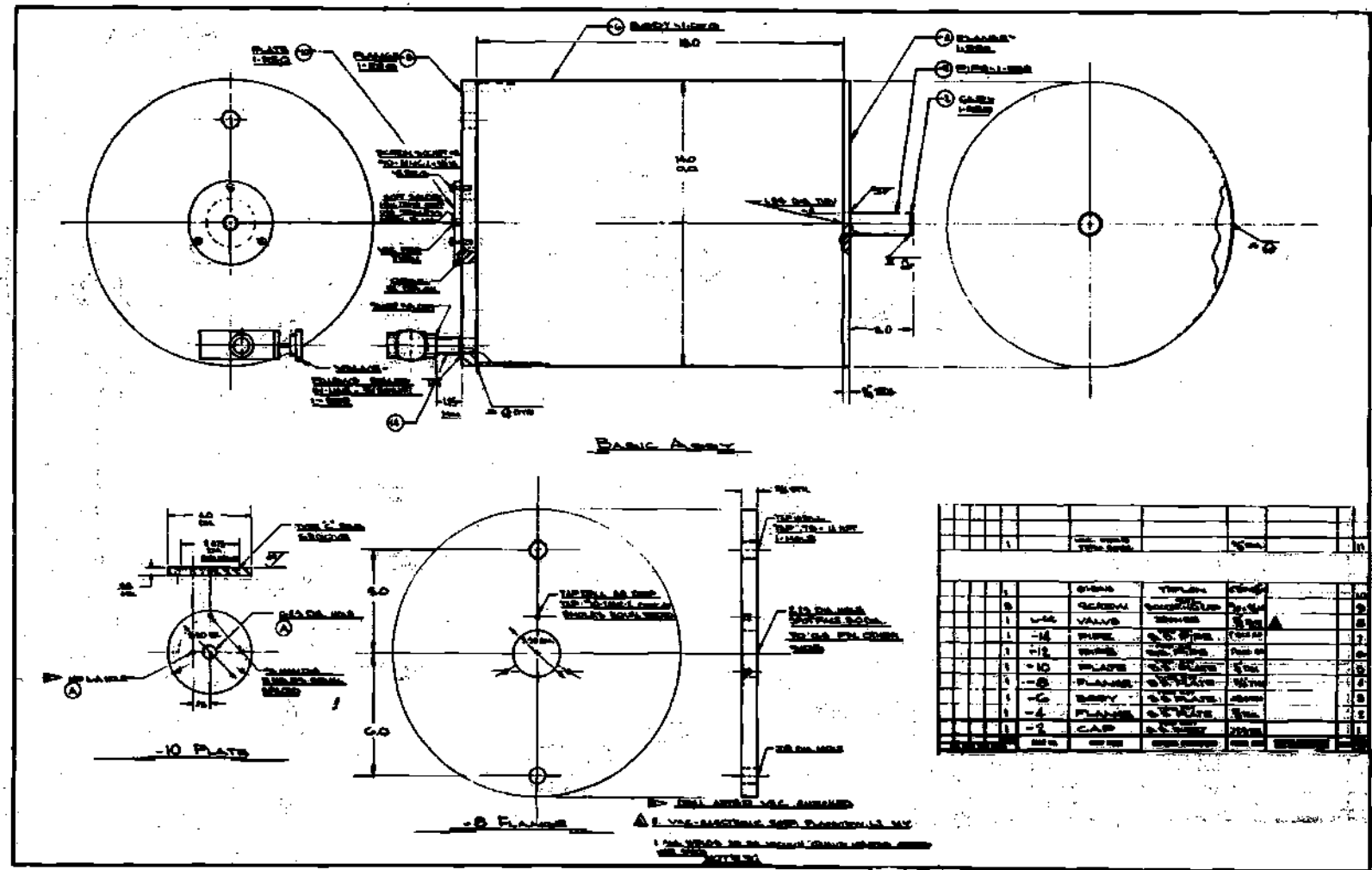

Figure 6. Machine Drawing Tank 1

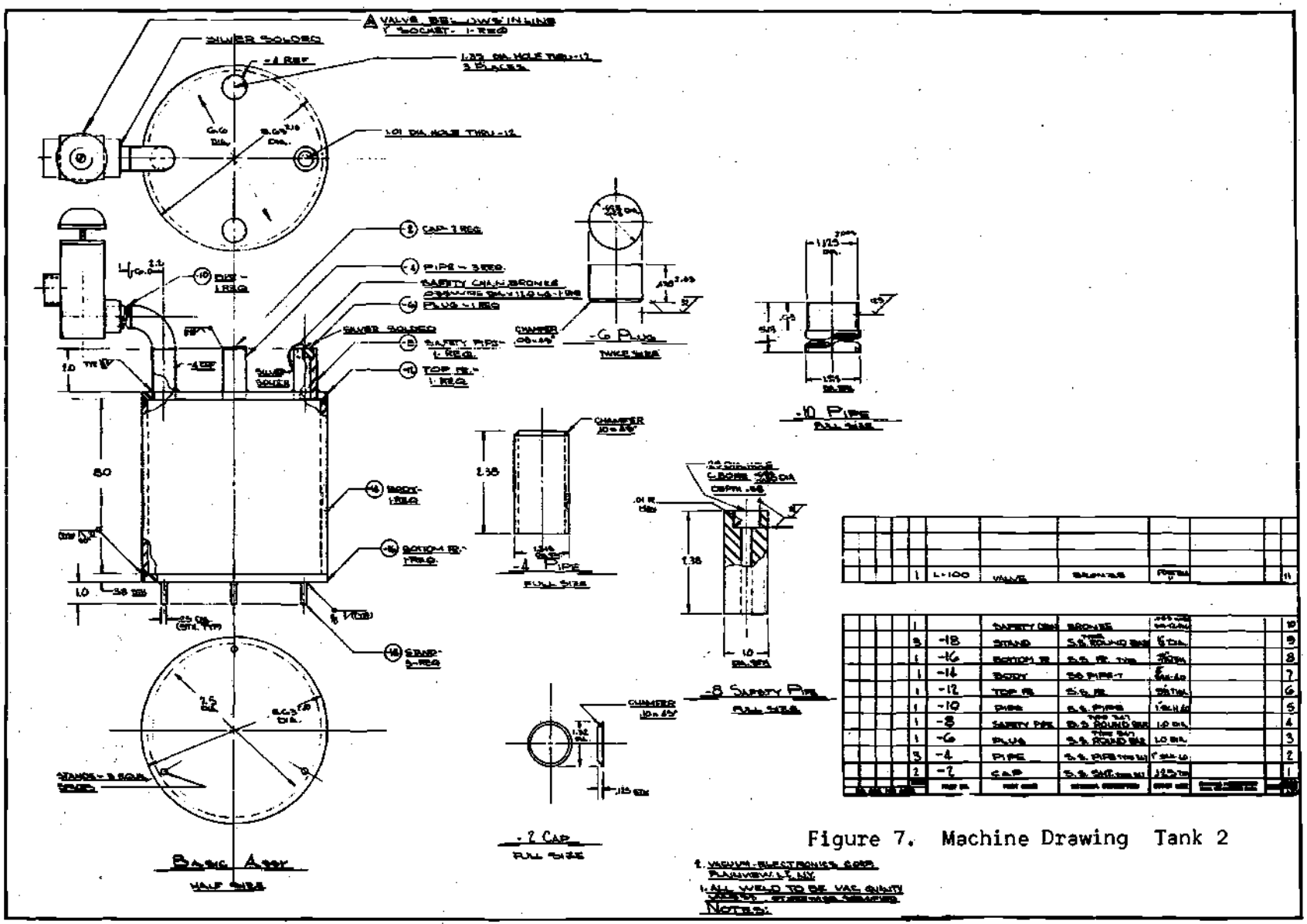

Figure 7. Machine Drawing Tank 2

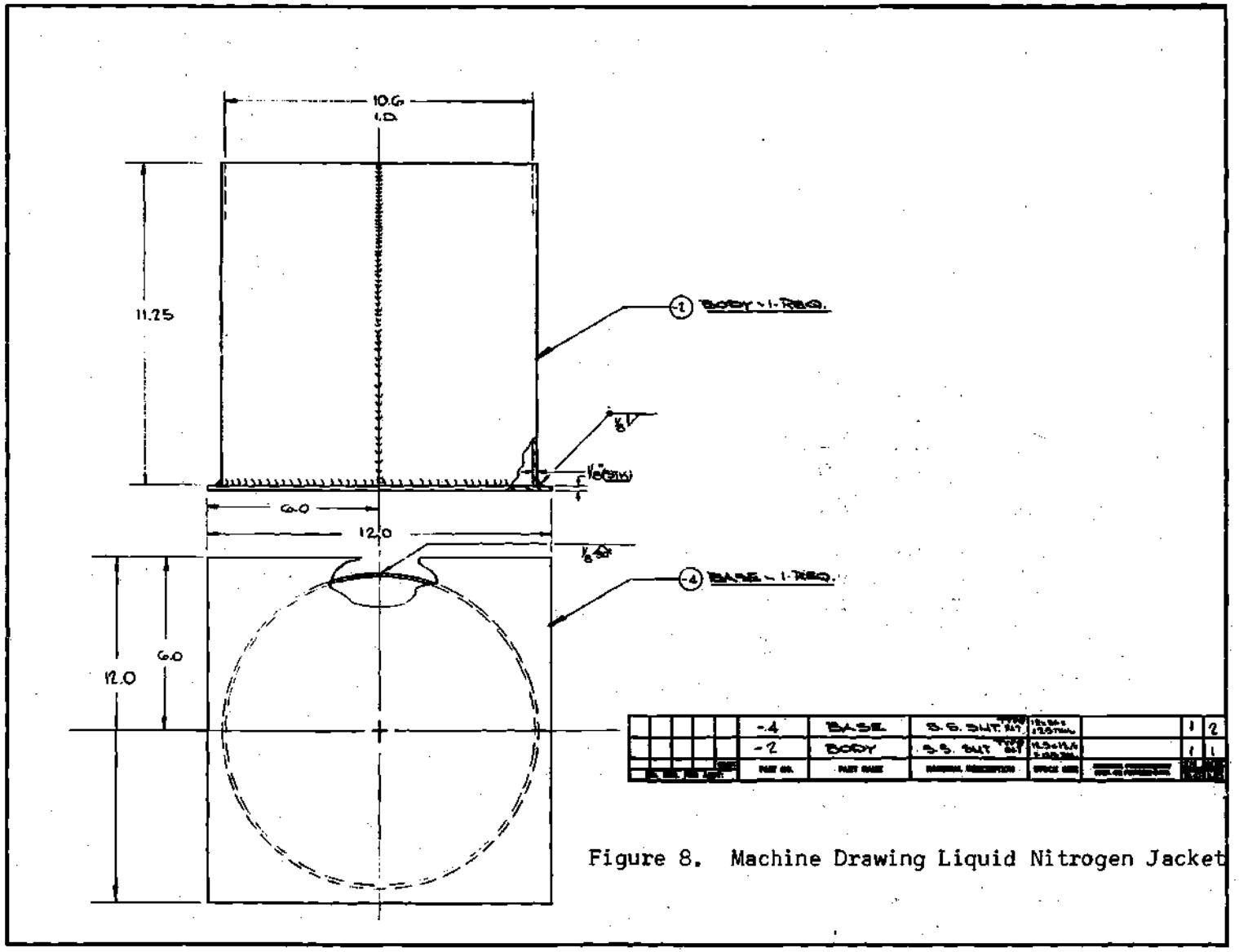

Figure 8. Machine Drawing Liquid Nitrogen Jacket

Commercial Humidity Instrumentation

The commercial humidity element used was a Phys-Chemical Research Corporation model number 11 humidity transducer. A photograph of the transducer appears in Figure 10. The transducer is located inside tank I with the detector wires fed to it through the port hole cover in tank I (see Figure 5).

The transducer is made of a non-conducting sheet which has impregnated into its surface a hygroscopic salt. The resistance of this salt is dependent on the water content of the salt; and, thus, a calibration can be obtained of water vapor content versus humidity transducer resistance. At the low humidities encountered in a vacuum, the resistance of this transducer is extremely large (in the range of 100 meg ohms). Due to the fact that a direct current would cause polarization of the transducer, some type of alternating current detection device must be utilized. To measure the pure resistance of the transducer with a resistance detector that operates on alternating current is extremely difficult at the operating range of impedance of the transducer. This can be explained with the aid of Figure 9 where R_x, C_x, and E_x are the transducer resistance, capacitive impedance, and detector imput voltage respectively.

The equivalent impedance between electrodes is given by

$$Z_{equi} = \frac{C_x}{C_x + R_x} \tag{3.1}$$

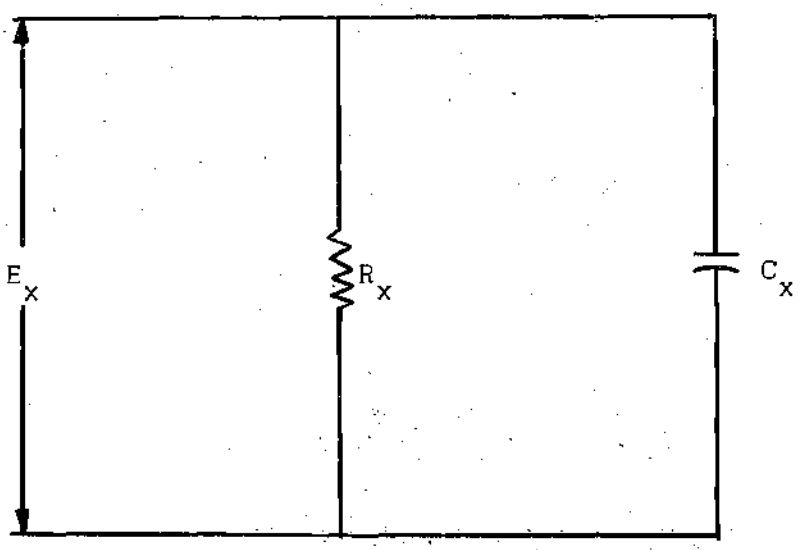

Figure 9. Electrical Schematic of Humidity Transducer

If the numerator and denominator of equation 3.1 are divided by R_x, the following relation for the impedance is obtained:

$$Z_{equi} = \frac{C_x}{\frac{C_x}{R_x} + 1} \tag{3.2}$$

At very low humidities where $C_x \ll R_x$, equation 3.2 simplifies to the following:

$$Z_{equi} = C_x \tag{3.3}$$

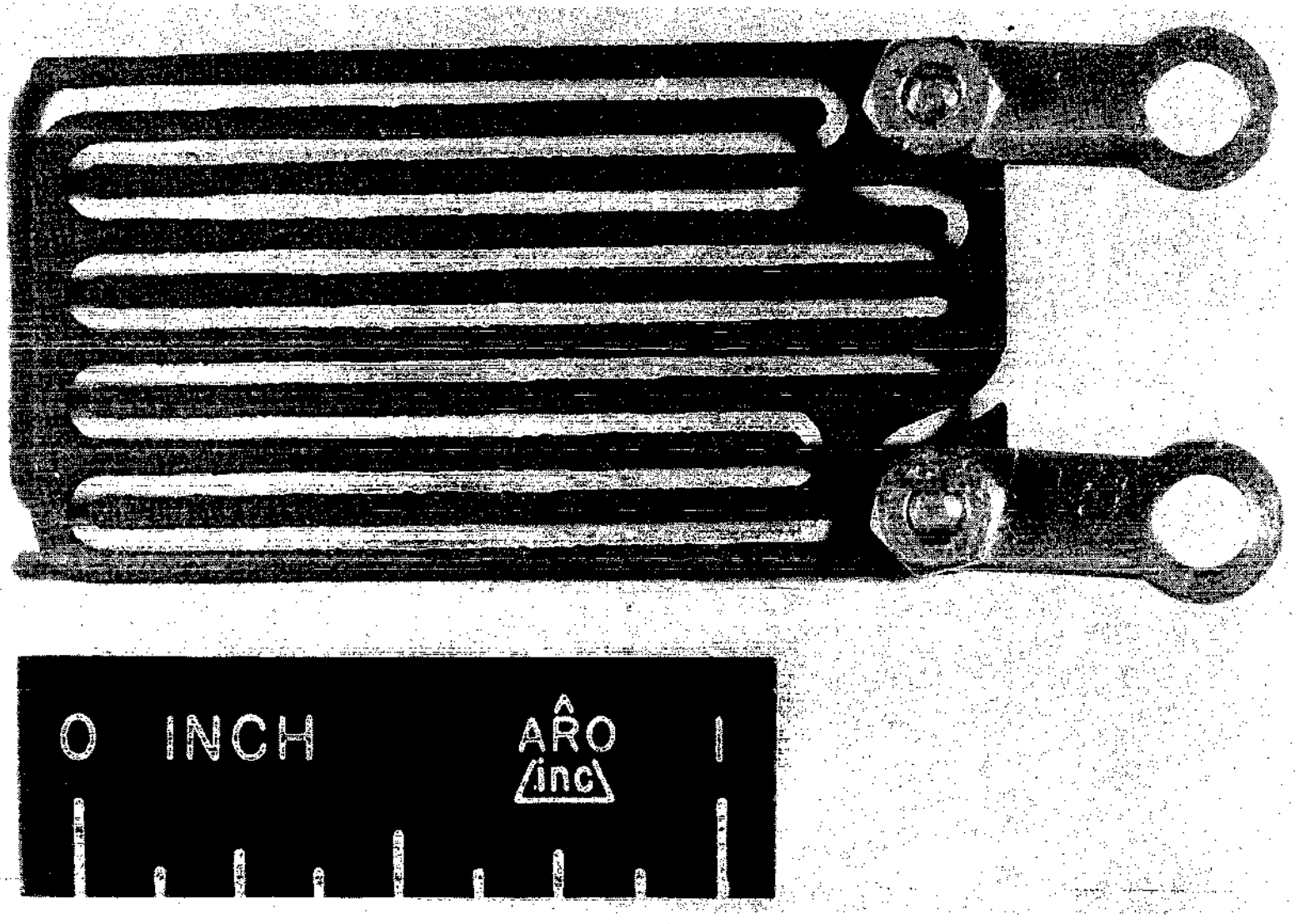

Figure 10. PCRC Model No. 11 Humidity Transducer

C_x is essentially constant for a given input frequency which means the transducer will reach a point where it has ceased to be sensitive to water vapor content and is producing an output which is a function only of the constant value of C_x and not the moisture condition. This demonstrates the capacitance limitation of the element at low humidities.

The circuit shown schematically in Figure 11 was found to be capable of detection up to 200 megohms at 60 cycles per second. Note that the capacitive effect of the transducer described above requires that for accurate measurement all noise effects be eliminated from the detector circuit. This was done by using standard shielded microphone wire to connect the transducer to the detector circuit. Also, the vacuum tube voltmeter was internally isolated to noise effects, and an isolation transformer was used to damp out disturbances in the voltage supply.

Each component used in the detector circuit is identified in Figure 11. The sensitivity of the vacuum tube voltmeter in the range used (0.0001 to 0.001 volts) was 0.00001 volts. The formula used for conversion of the output voltage of the vacuum tube voltmeter to humidity transducer resistance was as follows:

$$R_x = \left(\frac{10^s}{E_o} - 10^6\right) \div 10^6 \qquad (3.4)$$

The derivation of this formula appears in Appendix A.

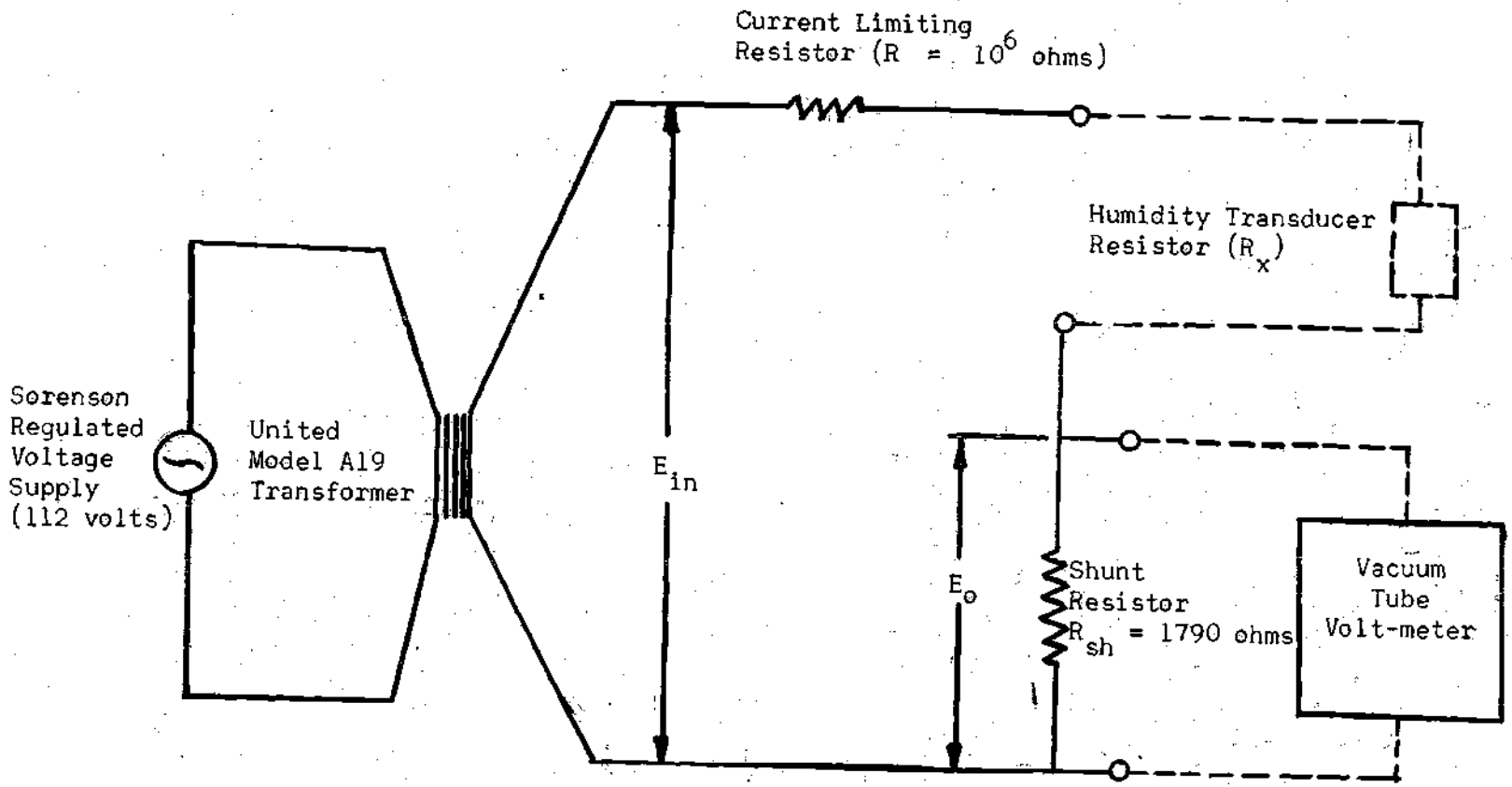

Figure 11. Detector Circuit

Pressure Instrumentation

For this work the most difficult measurement to make accurately was the pressure of the air-water vapor mixture in tank I. Most devices which are sensitive enough for the desired purpose are either damaged or affected in an unknown manner by the water vapor. For this work an NRC Equipment Corporation model number 520 alphatron gage was used. The head of the alphatron was mounted directly in the end flange of tank I (see Figure 4). ARO, Incorporated furnished a calibration curve for the gage for dry air, and the NRC Corporation gives for the ratio of the actual pressure to the pressure read for 100 per cent water vapor as 0.86. Also a linear interpolation is acceptable for any other percentage water vapor.

A Kinney model "Measurvac" McCleod type gage was used for measuring the pressure in tank II after the water was frozen from the sample. The gage was connected to tank II with a liquid nitrogen cold trap in the connecting line. The connecting line between tank II and the gage had a negligible volume compared to the volume of tank II. For the range used the gage had a sensitivity of 0.02 millimeters of mercury. ARO, Incorporated furnished a calibration curve for the entire pressure range of 0 to 760 millimeters of mercury.

Temperature Measurements

In this work temperatures at three different stations had to be measured:

1. The temperature inside tank I
2. The temperature inside tank II
3. The temperature of the ice in the "ice bulb" calibration attempt.

The temperature in tank I was measured with a copper-constantan thermocouple fabricated from Conax "metal clad" thermocouple cable, which consists of thermocouple wires tightly packed in a 1/8 inch outside diameter stainless steel tube with magnesium-oxide. The tube was cut back 1/2 inch and the thermocouple junction formed. A 1/8 inch hole was drilled in the port hole cover in tank I (see Figure 6), and the metal tube was fed through this hole to a depth of six inches and soft soldered in place.

Preliminary heat transfer calculations showed that with very good accuracy the temperature in tank II could be assumed equal to the liquid nitrogen temperature. The liquid nitrogen temperature was measured with copper-constantan thermocouple wire with a junction formed at the end of the wire.

Figure 12 is a drawing of the test section used in obtaining the "ice bulb" temperature. The thermocouple installation is essentially the same as the one described above for tank I.

The thermocouple output was recorded on a standard sixteen point "Brown" strip chart recorder manufactured by the Minneapolis Honeywell Corporation. It has a range of -350° F to 100° F with a sensitivity of 1° F. A calibration curve was furnished by ARO, Incorporated for the entire temperature range. The thermocouples with the strip chart recorder were calibrated by ARO using their primary temperature standards.

Experimental Procedure

Calibration of Humidity Transducer

The experimental procedure used to obtain the calibration curve

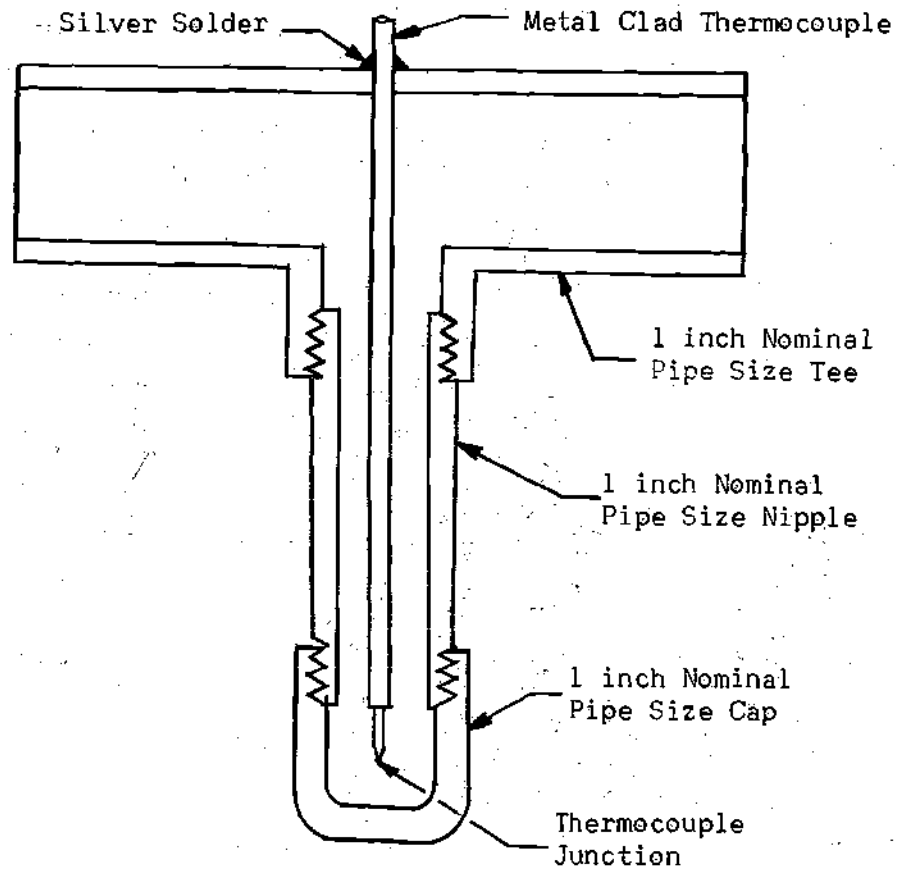

Figure 12. Ice Bulb Temperature Test Section

of humidity transducer resistance versus specific humidity, relative humidity, and partial density consisted of the following steps:

1. The power to the alphatron, resistance detector, strip chart recorder, and vacuum tube volt meter was turned on, and a minimum warm up time of one hour was provided.

2. Valves 1 and 2 (see Figure 5) were opened.

3. A five gallon cryogenic transport tank was filled with liquid nitrogen and made ready for use.

4. The cryogenic container for the liquid nitrogen cold trap was filled.

5. If a high humidity condition was desired, the line connecting tank I and tank II was disconnected and approximately a teaspoon of distilled water was introduced into tank I. This line was then connected.

6. The tanks were pumped to the desired pressure and valve 1 was closed. Care was exercised to allow all the liquid water introduced in step 5 to vaporize in order to insure equilibrium. This condition was determined by observing the alphatron gage. If there was a relatively rapid increase in pressure, this indicated the evaporation of liquid water; and this water was removed as indicated in the next step.

7. In generating the calibration curves, the humidity corresponding to a certain indicated resistance on the vacuum tube volt meter was required. If after the initial pumpdown performed in step 6, a lower humidity was desired to obtain the required resistance reading, the tanks were pumped to a lower pressure than attained in step 6. Air was introduced into the system at the point where the Kinney gage was

connected to the liquid nitrogen cold trap. This introduced essentially dry air into the system since the cold trap froze the water vapor from the atmospheric air. Many times the required condition was overrun (i.e. too much water was removed from the system) and steps 5 through 7 were repeated.

8. After the desired state point was obtained, readings of the alphatron were observed for a discernable change in pressure over a period of 20 minutes. If no change occurred in pressure then the system was assumed leak tight and valve 2 was closed.

9. The pressure in tank I, indicated by the alphatron, was recorded.

10. The temperature in tank I, indicated by the strip chart recorder, was recorded.

11. The voltage shown on the vacuum tube volt meter was recorded.

12. Liquid nitrogen was poured over tank II until it remained stable over the top of the tank at a depth of approximately 3/4 inches. Temperatures were allowed to equalize after this for approximately ten minutes.

13. After equilibrium had been achieved at the cryogenic temperature the pressure indicated by the Kinney McCleod gage was recorded. Also the liquid nitrogen temperature was recorded.

14. Drain 1 was opened and the liquid nitrogen was discharged.

15. Drain 1 was closed and hot water was poured over tank II to bring it to approximately room temperature. Several different immersions in hot water were required to bring this large mass to essentially room temperature.

16. The apparatus was allowed four hours to achieve thermal equilibrium with its surroundings.

17. Steps 1 through 16 were repeated for a new test.

"Ice Bulb Temperature"

The following steps were performed in attempting to calibrate the ice bulb temperature versus specific humidity:

1. The power to the alphatron, resistance detector, strip chart recorder, and vacuum tube volt meter was turned on, and a minimum warm up time of one hour was provided.

2. The ice bulb test section (see Figure 12) was filled above the thermocouple junction with distilled water and then placed in the line between tank I and tank II.

3. Valve 2 was closed.

4. The pressure in tank I was pumped down to the desired value. Valve 1 was adjusted so that the mass of water sublimed by the ice was pumped out of the system. This maintained a constant pressure in tank I.

5. The pressure in tank I indicated by the alphatron was recorded.

6. The temperature in tank I indicated by the strip chart recorder was recorded.

7. Readings of ice bulb temperature versus voltage on the vacuum tube voltmeter were taken simultaneously. (Note that the voltage reading was converted to specific humidity through the calibration curve previously obtained of specific humidity versus transducer resistance.)

Pressure Read Through a Liquid Nitrogen Cold Trap

The experimental work in determining the relationship of the partial pressure of dry air in an air-water vapor mixture and the pressure of the

mixture obtained through a cold trap was conducted along with the work done in obtaining a calibration curve of moisture content versus transducer resistance. The procedure used was to take the pressure of the air-water vapor mixture with the Kinney McCleod gage through a cold trap immediately after step 8 (see page 33). This pressure then could be compared with the partial pressure of the dry air obtained from the standard and to the total pressure of the mixture.

CHAPTER IV

PRESENTATION AND DISCUSSION OF RESULTS

Humidity Transducer Calibration

The calibration curves obtained for the PCRC model number 11 humidity transducer are shown for the three different pressures considered in Figures 13 through 15. Part of the range considered ($160 < R_x < 170$meg ohms) makes a linear plot when the reduced resistance ($R_x - 160$) is plotted against specific humidity in a semi-logarithmic plot as is indicated in Figure 16. An attempt to obtain a linear plot for the range $170 < R_x < 180$ megohms was not successful, and the failure can be attributed to the fact that the capacitive effect of the transducer is beginning to dominate in this range. This effect is explained in Chapter III.

An equation is desired which will give the specific humidity as a function of reduced resistance for all pressures in the range 1.9 to 5.47 millimeters of mercury. The following method is used to produce the desired result:

1. Apply to each line in Figure 16 the equation of a straight line

$$y - y_1 = S\,(x - x_1) \tag{4.1}$$

where "y" and "x" are the variables measures along the ordinate and

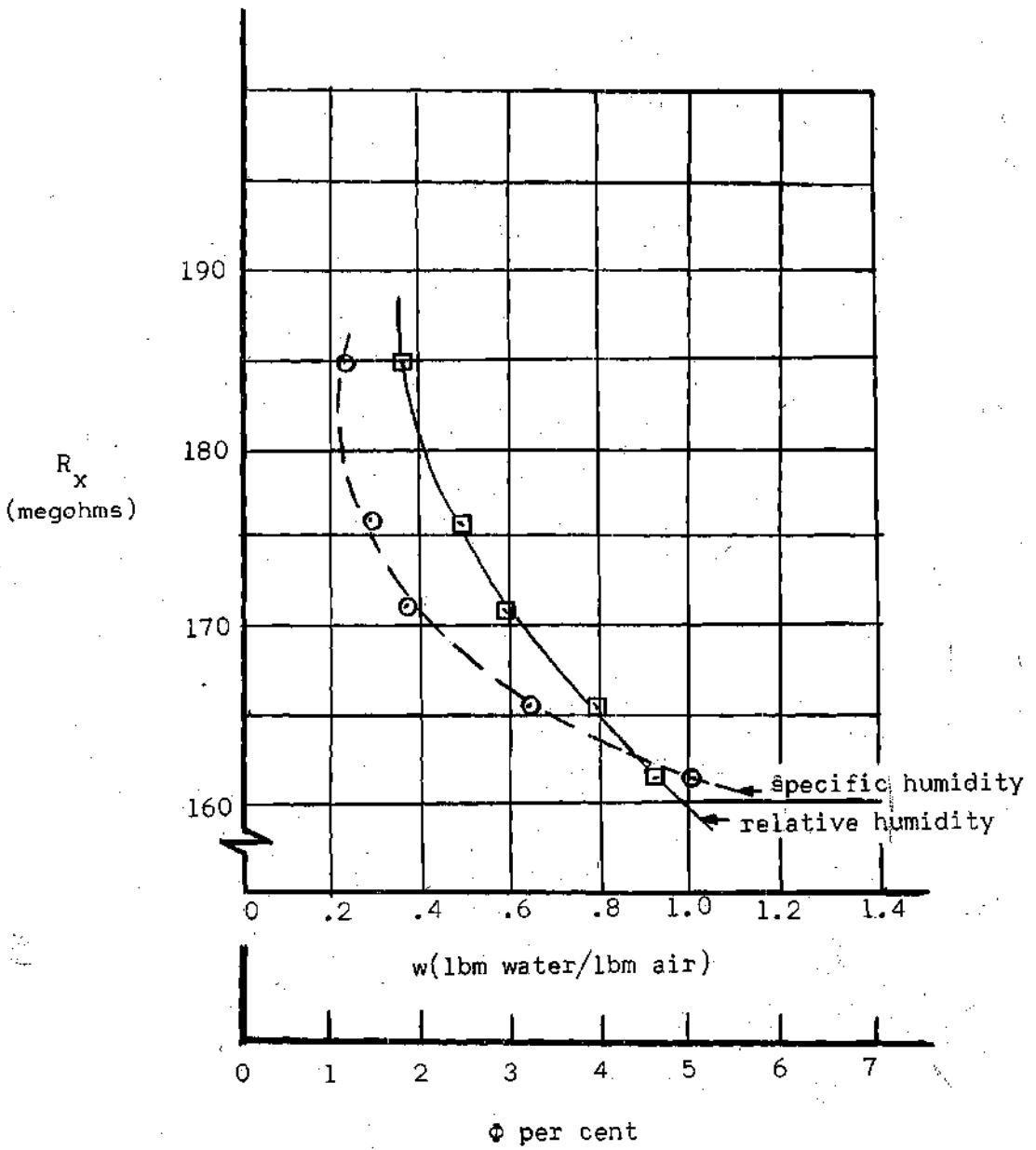

Figure 13. Specific and Relative Humidity Versus Transducer Resistance (P = 1.9 mm of Hg)

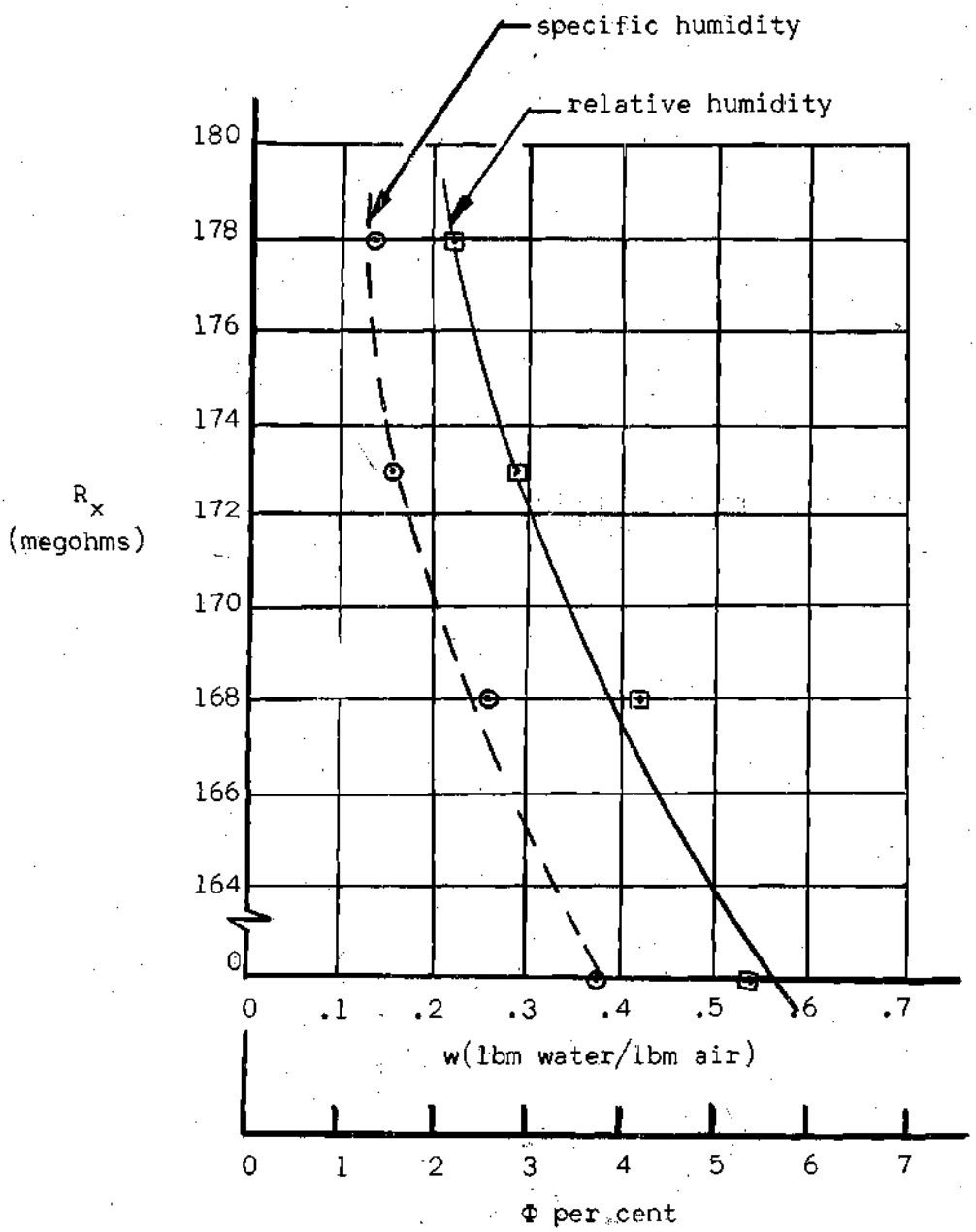

Figure 14. Specific and Relative Humidity versus Transducer Resistance (P = 3.5 mm of Hg)

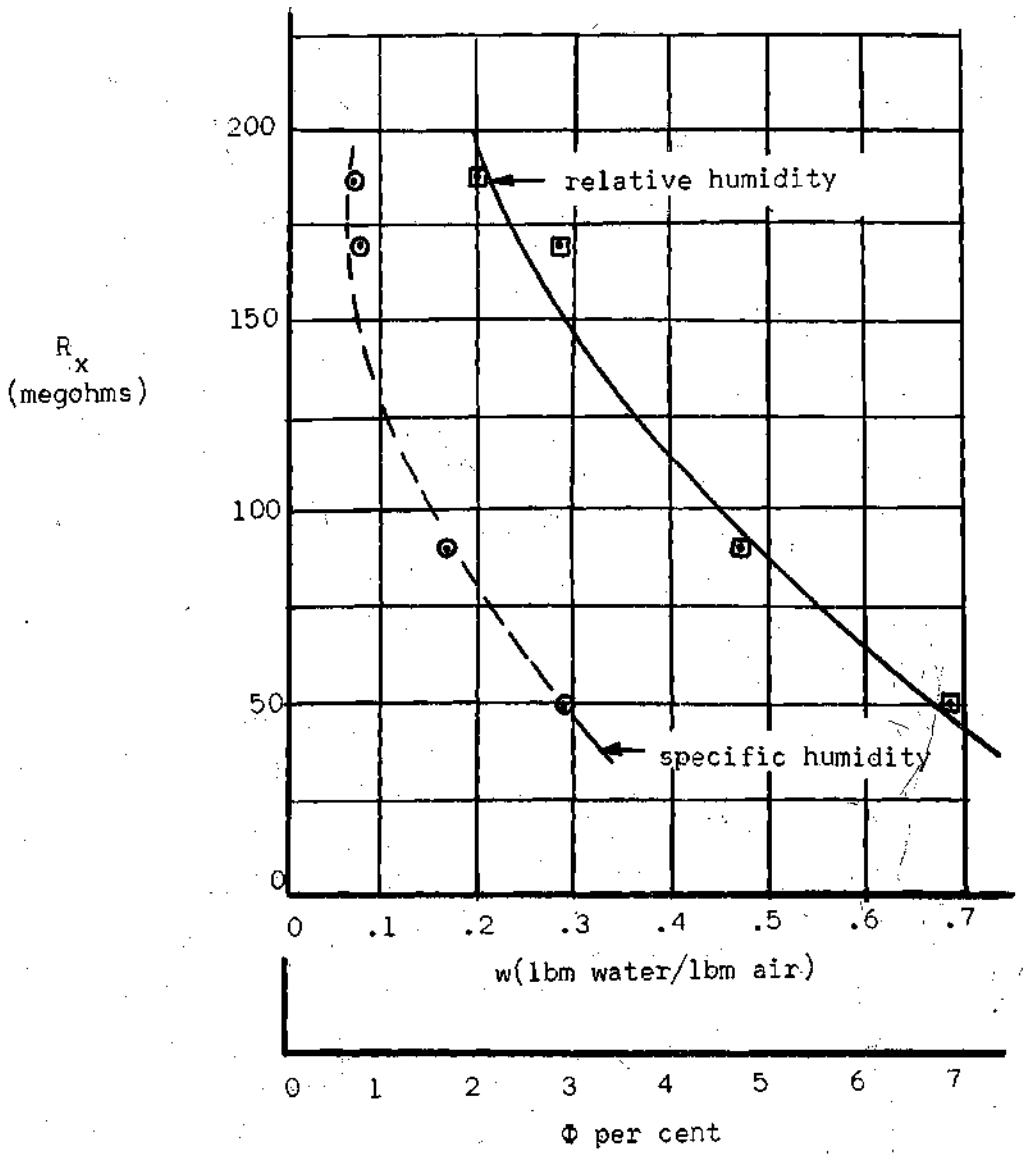

Figure 15. Specific and Relative Humidity versus Transducer Resistance (P = 5.47 mm of Hg)

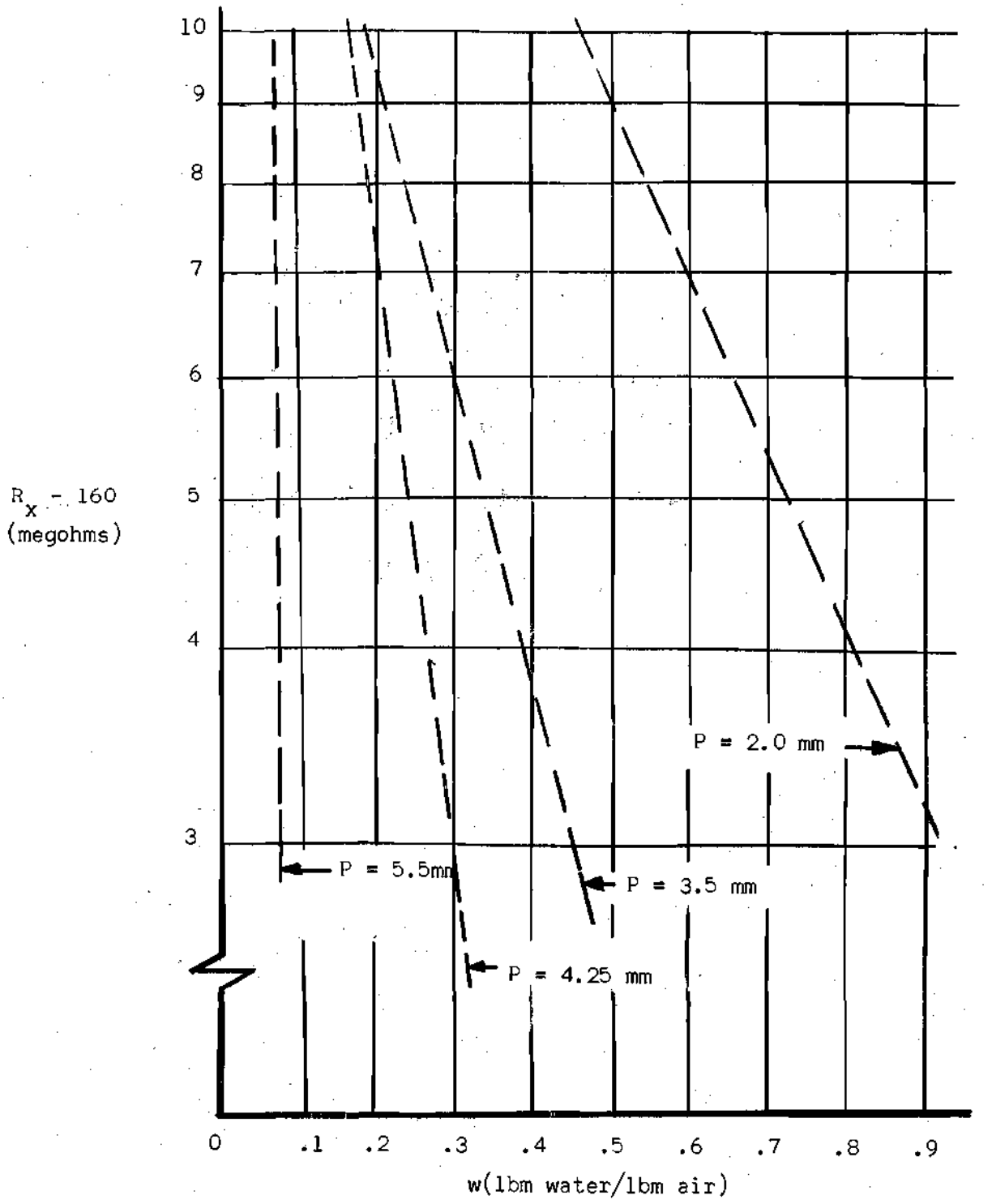

Figure 16. Reduce Resistance versus Specific Humidity

absissca respectively, "s" is the slope of the line, and "y_1" is a point of the ordinate corresponding to the point "x_1" on the absissca. The values for "s," "x_1," and "y_1" for the different curves in Figure 16 are summarized below.

Table 1. Coefficients of Equation 4.1

Pressure	s	x_1	y_1
5.47	-327.0	0.076	1.61
4.25	-9.30	0.290	1.61
3.51	-4.63	0.340	1.61
1.90	-2.61	0.730	1.61

Note that "y" corresponds to the $\ln(R_x - 160)$ and "x" to the specific humidity.

2. Rearrange equation 4.1 for each line in Figure 16 to the following form:

$$w = \frac{A(p) - \ln(R-160)}{B(p)} \qquad (4.2)$$

The values of A(p) and B(p) for each line in Figure 16 are tabulated below in Table 2. From the values tabulated in Table 2, a curve of A(p) and B(p) is drawn versus pressure in Figure 17. Consequently, the

specific humidity can be calculated from equation 4.2 by measuring the pressure of the sample under consideration and the resistance that it produces in the humidity transducer, and using Figure 17 to determine the values of A(p) and B(p).

Table 2. Pressure Coefficients

Pressure	A(p)	B(p)
5.47	26.51	327
4.25	3.95	9.3
3.51	3.185	4.63
1.90	3.515	2.61

Although the curves appearing in Figures 13 through 15 are quite useful in the approximate pressure range of 2 to 5.5 millimeters of mercury, a more desirable curve would be a plot of resistance versus some parameter which included all the quantities which affect the resistance such that a single curve could be used for all pressures and temperatures. A plot of transducer resistance versus the partial density of the water vapor was made and shown in Figure 18 for the various pressures checked. Note that all these measurements were made at 78° F, and from the ideal gas law (equation 2.1) it is seen that at a constant temperature the partial density is a function only of the partial pressure of the water vapor. From Figure 18 it is seen that the partial density and, thus,

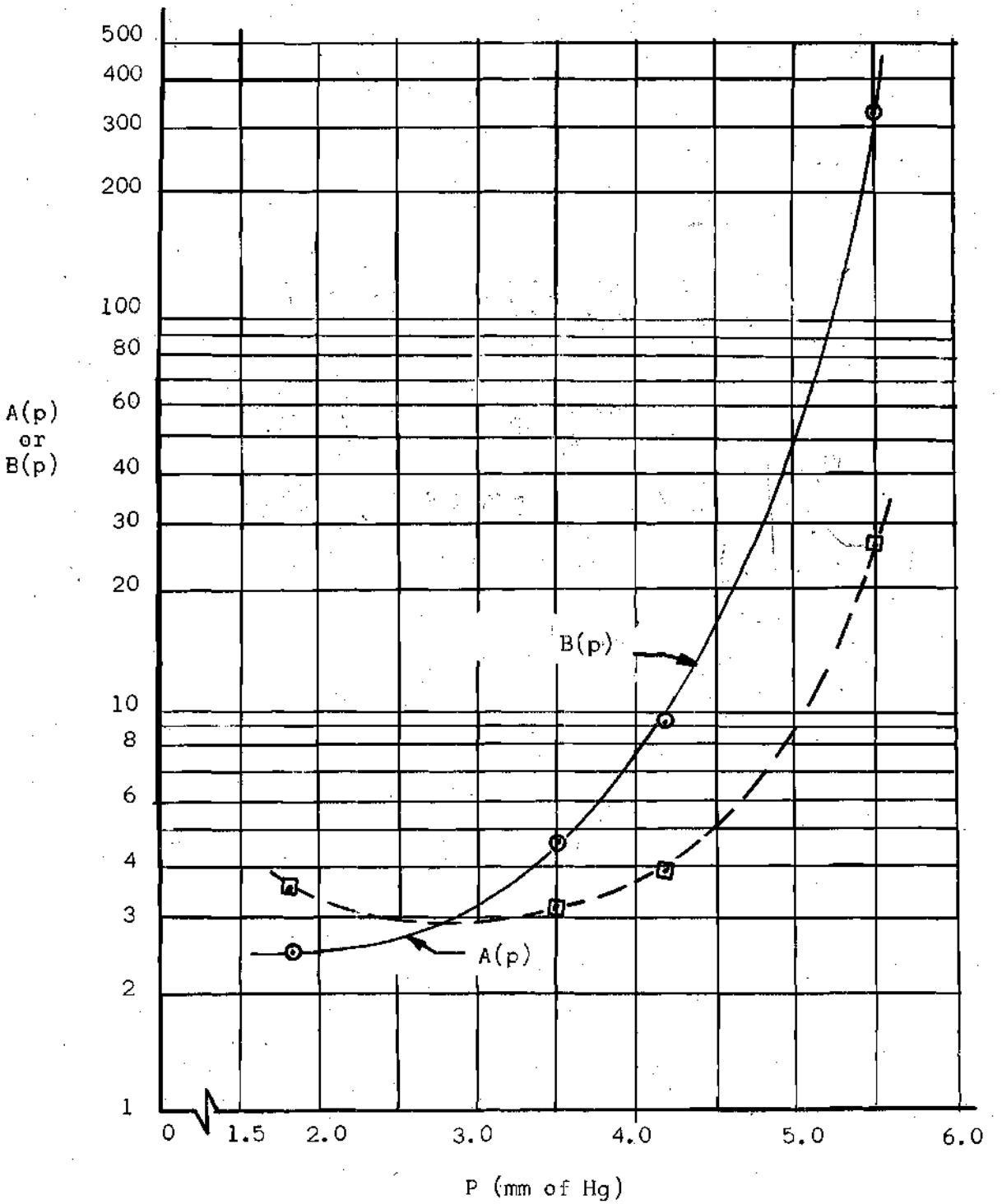

Figure 17. Pressure Coefficients

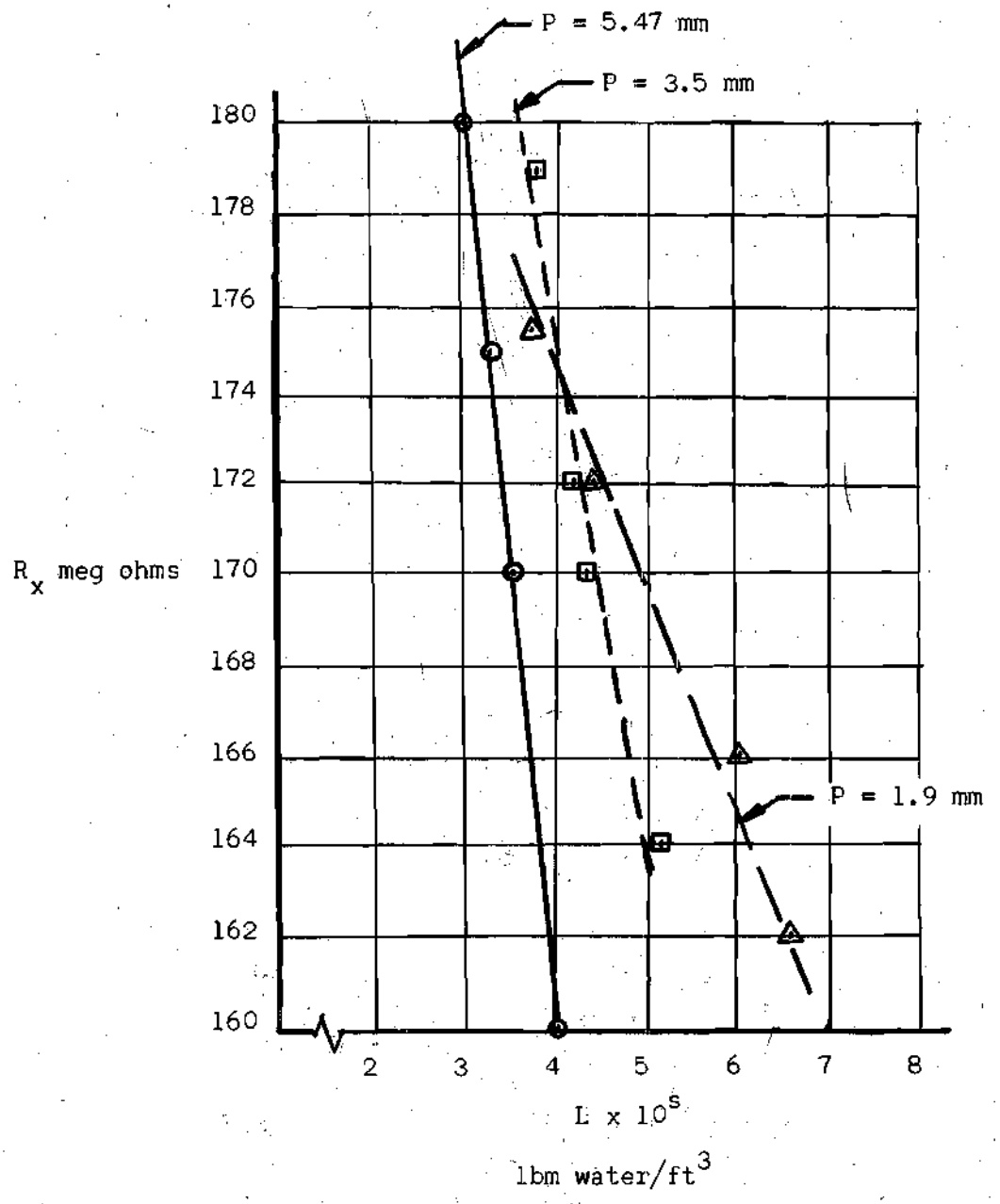

Figure 18. Partial Density versus Resistance
P = 1.9, 3.5, 5.47 mm of Hg

the partial pressure of the water vapor is not the only quantity affecting the amount of moisture in the material. Also from Figures 13 through 15 it is seen that the resistance is not solely a function of the specific humidity or relative humidity. No single parameter has been found which would predict this equilibrium moisture content. In fact, no satisfactory analytical predictions of equilibrium moisture content have been made (see reference (5)).

It should be noted that only two points in Figure 18 (those on the 1.9 millimeter of mercury pressure line) show an irregularity in correlating the transducer resistance versus the partial pressure of the water vapor. The experimental data for these two points could be in error but without additional data it must be concluded that additional factors are controlling the water content of the transducer material.

All of the calibration curves shown for the transducer were made at a temperature of 78° F. The transducer is slightly temperature sensitive. The Phys-Chemical Research Corporation gives as the temperature coefficient of the gage 0.2 per cent relative humidity change per °F temperature change. To check this temperature coefficient an air-water vapor sample was isolated in a tank at 3.6 millimeters of mercury total pressure. The temperature of the mixture was varied from 63 to 93° F and the humidity transducer reading was observed. The transducer showed a negligible change in resistance over this temperature range. At first consideration this result would seem inconsistent with the temperature coefficient given by the Phys-Chemical Research Corporation. However, the following example shows that this is not the case.

Consider a tank which has a fixed volume "V" initially containing an air-water vapor mixture at a temperature, total pressure, and specific humidity of 78° F, 3.16 millimeters of mercury, and 0.31 lbm of water per lbm of air respectively. Heat is transferred from the system leaving the composition and volume the same but lowering the final temperature to 65° F. The initial and final relative humidity is required. First applying the equation for specific humidity given by reference (6)

$$w = .622 \frac{\bar{P}_w}{P_i - \bar{P}_w} \tag{4.3}$$

$$P_i = 3.6 \text{ mm Hg } .01938 \text{ lb/in}^2/\text{mm Hg} = .0695 \text{ lb/in}^2.$$

Substituting P_i into equation 4.3 and solving

$$\bar{P}_{wi} = .0232 \text{ lb/in}^2 \quad .$$

After the temperature of the mixture reaches 65° F

$$\bar{P}_{wf} = \frac{m_{wf} R_w T_f}{V} \quad . \tag{4.4}$$

From the ideal gas law

$$m_{wf} = \frac{\bar{P}_{wi}\, V}{R_w\, T_i} \tag{4.5}$$

Substituting equation 4.4 into equation 4.5 and solving

$$\bar{P}_{wf} = P_{wi}\frac{T_f}{T_i} = .0232 \text{ lb/in}^2 \frac{525^\circ \text{ R}}{538^\circ \text{ R}} = .0218 \text{ lb/in}^2$$

Using the equation for relative humidity given by reference (6), the initial and final relative humidity can be calculated.

$$\Phi_i = (\bar{P}_{wi}/P_{si})100 = (.0232/.4747)100 = 4.9 \text{ per cent}$$

$$\Phi_f = (\bar{P}_{wf}/P_{sf})100 = (.0218/.3056)100 = 7.2 \text{ per cent}$$

Thus, it is seen that with a constant specific humidity, the relative humidity will still change with temperature.

The example just cited was the one considered experimentally for which there was negligible change in resistance even though there was a temperature change. This experimental finding can be seen to be consistent with the PCRC temperature coefficient because the calculated relative humidity change for this case was 2.3 per cent while the change in relative humidity calculated from the temperature coefficient for this same case is 2.6 per cent. The error in the final relative humidity calculated by using the PCRC temperature coefficient

would be approximately 4 per cent. These results show that the effect of temperature on the calibration curve of resistance versus relative humidity can be accounted for by use of a temperature coefficient of 0.2 per cent relative humidity per $^{\circ}$F temperature change. From another view point, this example shows that for small temperature deviations ($\pm 15^{\circ}$ F) the effect of temperature on the calibration curves of resistance versus specific humidity is negligible.

Use of the Cold Trap for Determination of the Dry Air Parial Pressure

It has been recently reported in reference (7) that the pressure of an air-water vapor mixture read through a cold trap is the partial pressure of the dry air in the air-water vapor mixture. This reference dealt with measurements made in the micron range of pressure.

This finding was checked in the 1 millimeter of mercury pressure range. Although the pressure instrumentation which was used was not sensitive enough to indicate the exact relationship between the pressure read, the total pressure, and the partial pressure of the dry air, a general trend was determined which is depicted in Figure 19. These findings show, as Figure 19 indicates, that the pressure read lies somewhere between the total pressure and the partial pressure of the dry air.

"Ice Bulb Temperature"

The use of the equilibrium temperature of ice surrounded by a low vacuum air-water vapor mixture was also checked as a possibility for a humidity indicating instrument. Although this device showed a sensitivity to environmental moisture content, the results of this

work were inconclusive due to the lack of control over the other factors affecting the equilibrium temperature such as external heat transfer and environmental conditions adjacent to the ice cube. An indication of the sensitivity and drift in the readings of this ice temperature is indicated in Figure 20 which consists of two sets of actual measured values.

The use of a device of this type to measure small volumes of a low density air water vapor mixture appears to be impractical since the subliming ice would continually change the environmental conditions. Also, the other factors governing the ice temperature are difficult to control accurately. For measurement of moisture in a low density flow of an air water vapor mixture the device has some merit since equilibrium could be more easily reached under these conditions.

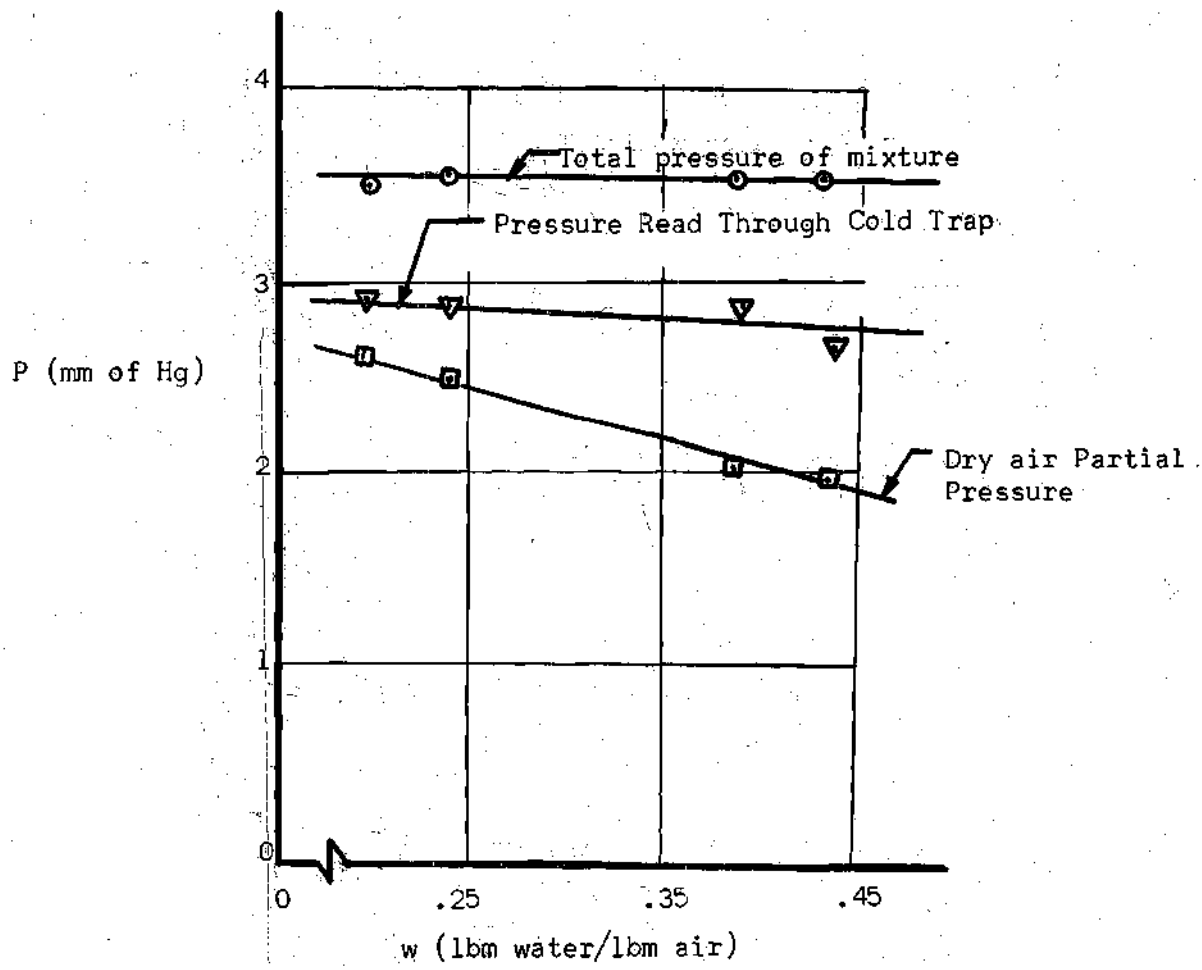

Figure 19. Relationship of Partial Pressure of Dry Air to Pressure Read Through Cold Trap

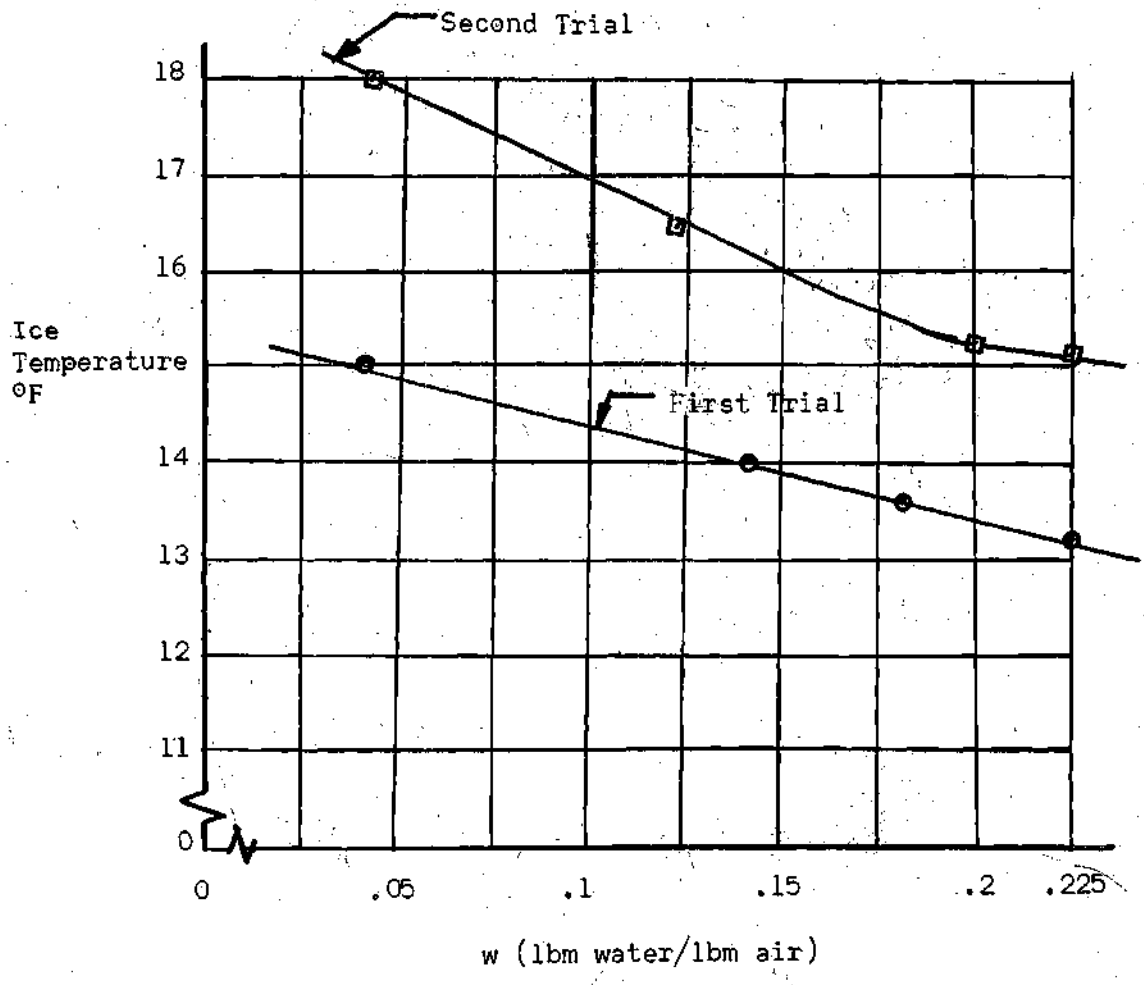

Figure 20. Ice Bulb Temperature

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

An experimental investigation has been made into the determination of water vapor content under low vacuum conditions by three different methods which are as follows: the electrolytic hygrometer, the ice bulb temperature, and the reading of the pressure of a mixture through a cold trap.

The conclusions drawn from this investigation are:

1. An electrolytic hygrometer can be successfully used under low vacuum conditions (see for example Figure 13). The hygrometer tested, a PCRC model number 11 humidity transducer, has a temperature sensitivity of .2 per cent relative humidity per degree F in the temperature range 63 to 93° F. The effect of pressure on the transducer can be accounted for by using equation 4.2 in conjunction with Figure 17. The maximum probable error of the calibration curves for the instrument is 5 per cent.

2. The equilibrium temperature of ice in contact with an air-water vapor mixture is sensitive to the moisture content of the mixture, but this temperature is affected by several other factors which would have to be much more carefully controlled than in this work for a successful calibration. Also the sublimed water added to the air water vapor mixture continually changes the environmental conditions.

3. The result reported in reference (7) indicating that in the micron range the pressure read through a cold trap of an air-water vapor mixture is the dry air partial pressure is found not to hold in the millimeter of mercury pressure range.

The following items are recommended as a logical extension of the work which has been presented:

1. Improvement of the pressure instrumentation would allow the exact determination of the relationship between the partial pressure of air in an air-water vapor mixture, the total pressure of the mixture, and the pressure of the mixture read through a cold trap. Further analytical and experimental work needs to be done in this area.

2. A parameter should be determined such that for any pressure, temperature and composition of mixture, a plot of this parameter versus resistance of the humidity transducer involving the equilibrium moisture content of a material for which little analytical work has been done.

3. In order to eliminate the problem of alternating current detection of resistance at extremely high resistances a special transducer to replace the one used for this work should be fabricated and calibrated for low vacuums. The Phys-Chemical Research Corporation can custom fabricate this type transducer.

APPENDIX A

TRANSDUCER RESISTANCE AS A FUNCTION OF DETECTOR VOLTAGE

The following derivation is given for the formula which will convert the voltage readout of the humidity transducer impedance detector to resistance. Refer to Figure 11 for definition of symbols.

From Ohm's law assuming infinite impedance of the vacuum tube voltmeter the following equation can be written:

$$I = \frac{E_{in}\ (10)^6}{1.0 + R_x + R_{sh}} \qquad A.1$$

and

$$E_o = I\ R_{sh} \div 10^6 \qquad A.2$$

Substituting A.1 into A.2 the following is obtained:

$$E_o = \frac{E_{in}\ R_s}{1.0 + R_x + R_{sh}} \qquad A.3$$

Rearranging gives the following form:

$$1.0 + R_x = \frac{E_{in} - E_o}{E_o} \cdot R_{sh} \qquad A.4$$

Assume that $R_{sh} \ll 1$ meg ohm, and $E_o \ll E_{in}$ which gives the following equation from equation A.4:

$$1.0 + R_x = \frac{E_{in}}{E_o} R_{sh} \qquad A.5$$

Arbitrarily for $R_x = 0$ let $E_o = 0.1$ volt. The voltage supplied by the transformer was 56.0 volts. Substituting the values in A.5 gives

$$R_s = \frac{10^6(.1)}{56} = 1.790 \times 10^{-3} \text{ meg ohms}$$

The equation for R_x then becomes

$$R_x = \left\{\frac{10^8}{E_o} - 10^6\right\} \div 10^6 \qquad A.6$$

APPENDIX B

SAMPLE CALCULATIONS

The following experimental data was obtained during one run:

1. P_1 = 5.55 millimeters of mercury
2. P_2 = 1.34 millimeters of mercury
3. T_1 = 538° R
4. T_2 = 141° R
5. E_o = 0.000538 volts

The following is a sample calculation using the above data for the relative humidity, specific humidity, partial density, and transducer resistance.

Relative Humidity

From equation 2.9

$$\Phi = \frac{P_1 - P_2 \frac{T_1}{T_2}}{P_s} 100$$

Substituting in values

$$\Phi = \frac{5.55 - 1.34 \frac{538}{141}}{24.5} = 1.83 \text{ per cent}$$

Specific Humidity

From equation 2.13

$$w = .622\left[P_1T_2/P_2T_1 - 1\right]$$

Substituting in experimental values the following is obtained:

$$w = .622\left[\frac{5.55}{1.34}\frac{141}{538} - 1\right] = .054$$

Partial Density

From equation 2.15

$$L = .01168\left[P_1/T_1 - P_2/T_2\right]$$

Substituting in experimental values and noting that specific humidity is not a dimensionless quantity so that the pressure must be converted to lbf/ft^2 by the conversion factor 2.79 $lbf/ft^2 \cdot$ mm of Hg, the following is obtained:

$$L = .01168\left[\frac{5.55}{538} - \frac{1.34}{141}\right] 2.79 = 2.6 \times 10^{-5} \text{ lbm/ft}^3$$

Electrical Resistance

From equation 3.4

$$R_x = \left\{\frac{10^5}{.000538} - 10^6\right\} \div 10^6 = 185 \text{ meg ohms}$$

APPENDIX C

ESTIMATED ERRORS

The estimation of error for the various instruments used in this study are listed in Table 3.

Table 3. Instrumentation Error

Type Instrument	Percentage Error
Thermocouples (all)	1.0
Alphatron Gage	4.0
Kinney Pressure Gage	2.0
Vacuum Tube Volt Meter	0.2

Reference (4) gives the maximum probable error for the following mathematical forms:

if

$$V = X \pm Y$$

then

$$\text{Maximum Probable Error} = \sqrt{Sx^2 + Sy^2}$$

if

$$V = XY \text{ or } X/Y$$

then

$$\text{Maximum Probable Error} = \sqrt{Sx^2 + Sy^2}$$

Where S denotes the fractional error in the variable indicated by its subscript, V is a variable dependent on the independent variables X and Y. If the equations for the maximum probable error shown above are applied to equations 2.9, 2.12, 2.14, and 3.4 using the error estimates given in Table 1, the maximum probable error in the relative humidity, specific humidity, and partial density is found to be approximately five per cent while the error in reading the transducer resistance is negligible.

It should also be pointed out that the author made several random checks for repeatibility of the calibration work and in no instance found the error to be greater than that predicted in the error analysis above. In fact this was true even when a different Phys-Chemical Research Corporation model number 11 transducer was used. This indicates that this humidity transducer is highly stable and that the production tolerances for the transducer are very close.

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